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FOREWORD

This Final Technical Documentary Report covers all work performed under Contract AF 33(657)-7104 from 5 September 1961 to 31 December 1962. The manuscript was released by the author on 28 February 1963 for publication as an ASD Technical Documentary Report.

This contract with the W. R. Grace & Co., Research Division of Clarksville, Maryland, was initiated under ASD Project 7-838, "Reproducible Thermistor Refinement Program". It was administered under the direction of Lieutenant T. Bailey, Electronics Engineer, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Dr. M. C. Vanik of W. R. Grace's Washington Research Center, Inorganic Chemical Research Department, was the supervisor in charge. Others who cooperated in the research and in the preparation of the report were: Dr. M. G. Sanchez, Director of Inorganic Chemical Research Department; Dr. W. T. Barrett, Former Director of Inorganic Chemical Research; Mr. J. E. Herrera, Chemist, Inorganic Chemical Research Department; Mr. E. M. Glocker, Manager Research Statistics, Economic Evaluation Department; Mr. S. E. Ketner, Statistician, Economic Evaluation Department and Miss B. B. White, Assistant Librarian, Research Services Department.

This project has been accomplished as a part of the Air Force Manufacturing Methods Program. The primary objective of the Air Force Manufacturing Methods Program is to develop, on a timely basis, manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas:

    Rolled Sheet, Forgings, Extrusions, Castings, Fiber & Powder Metallurgy,
    Component Fabrication, Joining, Forming, Materials Removal,
    Fuels, Lubricants, Ceramics, Graphites, Non-Metallic Structural Materials,
    Solid State Devices, Passive Devices, Thermionic Devices

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

FINAL REPORT ON REPRODUCIBLE THERMISTOR REFINEMENT PROGRAM

Milton C. Vanik

et al
W. R. Grace & Co.
Research Division

Gold-doped monocrystalline silicon exhibits temperature-resistivity
behavior suitable for making highly reproducible, predictable and
sensitive thermistors. Two types of thermistors were developed with
reproducibilities of ±2% and operable ranges including -85 to +200°C.
Manufacturing methods were developed and demonstrated on an unbalanced
pilot line.

A literature survey indicated that specially doped silicon or germa-
nium offer the best possibilities of being used as single-crystal
semiconductor thermistors. Silicon was chosen for development on
the basis of energy gap, purity, resistivity, and availability.

Many elements were screened as possible silicon thermistor dopants.
These include gold, copper, silver, nickel, iron, zinc, platinum,
manganese, and thallium. Only gold in both P- and N-type silicon
gave products suitable for use in the -85 to +200°C range.

Gold-doped N-type silicon produces a high resistivity thermistor
material with nearly linear log ρ vs $\frac{1}{T}$ response in the range
-85°C to +200°C. This material has a temperature coefficient of
resistivity of -7% per degree at 25°C. It is most suitable for
high temperature, narrow range, high sensitivity applications.

Gold-doped P-type silicon is a lower resistivity thermistor material
with linear log ρ vs $\frac{1}{T}$ behavior over the range of -85 to about
50°C. The temperature coefficient of resistivity of this material
is -4.5% per degree at 25°C.

A statistical study was completed comparing float-zone leveled
with diffused gold-doped thermistor silicon. The float-zone
leveling process produces the better product.

Pa.iii

Forming of ohmic and mechanically strong contacts to the thermistor silicon is extremely important. Stability of the thermistors is very dependent upon these contacts.

Manufacturing processes encompassing 24 steps for gold-doped N-type thermistors and 28 steps for gold-doped P-type thermistors have been established. An unbalanced pilot line was set up and operated according to these processes. A demonstration run was completed for the Air Force contract officer.

Six hundred samples were produced on this pilot line and sent to the Air Force for distribution. Many of these samples are within ±1% of a standard curve. All are within contract specifications of ±2%.

These thermistors should be useful in any application which calls for precise and/or closely matched thermistors.

****

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

JACK R. MARSH
Assistant Chief
Manufacturing Technology Laboratory
Directorate of Materials & Processes

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I INTRODUCTION

Conventional thermistors are now made from transition metal oxides
by ceramic techniques. These metal oxides are semiconductors. Their
electrical resistance decreases as they are heated. Dozens of other
semiconductor materials could conceivably be used in place of the
present thermistors as temperature-sensing devices. However, a
material that is to be selected for thermistor use should have ade-
quate sensitivity to temperature, reproducibility, and reliability.

Probably the purest and most reproducible semiconductor materials
available today are the large single crystals of silicon and germa-
nium that are used in the manufacture of electronic devices such as
transistors and diodes. Silicon crystals often contain electrically
active impurities as low as one ppb or less.

The objective of this project is the development of manufacturing
methods and the pilot plant production of thermally sensitive devices
which take advantage of the high reliability and reproducibility offer-
ed by large single-crystal semiconductors.

II DISCUSSION

1. Literature Search

A literature search has been completed covering all available information on thermistor element properites, thermistor element fabrication, and those properties of semiconductors applicable to temperature-sensing devices. A copy of this survey is attached in the appendix. This survey indicates that specially doped germanium and silicon offer the best possibilities of being used as single-crystal semiconductor thermistors. For instance, it points out that germanium doped with arsenic is a suitable low-temperature ($\sim$10°K or less thermistor[1]. When doped with iron, germanium produces a thermo-sensitive device operating from 0 to -200°C[2,3]. The temperature resistance behavior of manganese-doped germanium is described[4]. A straight line log resistivity versus 1/T relationship is obeyed in the temperature range of about 60°C to -140°C. Silicon doped with iron has been used in a thermally sensitive device operating in the -100° to +100°C range[5]. The resistivity of the iron-doped silicon is about 500,000 ohm cms at 25°C. A low-temperature thermometer (2° to 25°K) of copper-doped gallium arsenide is described[6]. Tantalum-doped aluminum antimonide also produces a thermistor material[7].

2. Evaluation of Single-Crystal Semiconductors as Thermistor Materials

Several criteria are necessary for a semiconductor material which is to be fabricated into a single-crystal thermistor operating in a temperature range of -85° to +200°C. The energy gap between the valence band and the conduction band should probably be greater than about 1 ev. Otherwise, appreciable intrinsic conduction might occur at temperatures below 200°C destroying any linearity in the conduction obtained by the introduction of resistivity-determining impurities. This would tend to eliminate germanium, indium arsenide, indium antimonide and gallium antimonide from the following list of single-crystal semiconductors:[8]

TABLE 1

	Eg(300°K) (ev)
Si	1.09
Ge	0.66
InP	1.27
InAs	0.33
InSb	0.17
GaP	2.25
GaAs	1.43
GaSb	0.70
AlSb	1.52

In germanium, for instance, intrinsic conduction could become appreciable at 100° to 125°C and interfere with the conduction obtained by introducing impurities that create the so-called deep-lying energy levels between the valence band and the conduction band.

If one considers purity of the monocrystalline semiconductors, including both resistivity-determining impurities and electrically inactive impurities, only germanium and silicon can be obtained in the parts-per-billion range. Silicon is considerably better than germanium in that respect. If one considers which of the above materials are readily available commercially, only silicon and germanium fit the bill. For the reasons mentioned above, we felt that properly doped silicon offered the best possibilities for making a thermistor with the properties described in the contract. Germanium was not eliminated from our consideration, however, and some experimental work was done with it.

3. Screening of Dopants in Silicon

In this laboratory we doped silicon with various impurities that
introduce energy levels between the valence and conduction bands of
silicon. In order to obtain conduction resulting from energy gaps on
the order of 0.2 ev or higher, it was necessary to dope with impurities
that introduce the so-called deep-lying impurity levels. The normally
used Group III and Group V elements which introduce shallow levels
(less than about 0.1 ev) were not used except in conjunction with the
deep-lying levels. We began a process of screening dopant materials
which might introduce the desired deep-lying energy levels.

Most of the screening was done by float-zone leveling techniques.
By this technique, impurities which have a low segregation coefficient
(such as most of the dopants in which we were interested) can be added
in a very uniform manner to a silicon rod during the float-zone process.
A single crystalline rod of known resistivity is mounted in a zone
refiner and butted against a seed of known resistivity. The dopant is
weighed in at the seed rod junction, fused into the first zone, and
then passed thru the rod with the zone. As the zone traverses the
length of the rod, an essentially constant level of impurity is left
behind. The distribution coefficient of an impurity in float-zone
refining is the ratio of the impurity in the crystallizing solid to
the amount in the molten zone. If the distribution coefficient is small,
gold is about 3×10^{-5}, the amount that crystallizes from the zone is so
small compared to the amount in the zone that the quantity in the zone
essentially remains constant throughout a pass. Hence the amount of
impurity left in the rod at any point is essentially constant.

Other techniques which are used to add impurities were crystal
pulling and diffusion techniques. When pulling a crystal by the
Czochralski technique and using a dopant with a low distribution
coefficient, the impurity left in the crystal is inversely proportional
to the fraction of the melt remaining. For instance, when 25% of the
melt has been crystallized, the amount of impurity in the crystal at
that point is two-thirds the amount of impurity in the crystal when
50% of the crystal has crystallized. This technique is therefore
useful in determining the effect of varying amounts of dopant upon the
temperature-resistance characteristics of a material. Diffusion was
used mainly for doping silicon with gold. Diffusion was carried out
in an argon ambient at 1200°C. If reasonable diffusion times are to
be realized, the diffusion rate of the impurity in the substrate must
be relatively fast. Such is the case of copper and gold in silicon.

Elements which were screened as dopants for thermistor silicon
include gold, copper, silver, nickel, iron, zinc, platinum, manganese,
and thallium. Only the highest-purity spectrographic- or electronic-
grade dopants were used. No erratic behavior was noted from contami-
nation of the dopants with impurities with segregation coefficients
close to one. One would expect to see the effect of a contaminant
such as boron (distribution coefficient~0.8) and phosphorus

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(distribution coefficient 0.3) at the seed end of the crystal since only one pass is given in the float-zone leveling process. For most of the dopants which have distribution coefficients on the order of 3×10^{-5}, 0.1 gram added to the initial zone of a 15/16" rod results in a residual rod concentration of about 20 ppb. This is based on the estimate of the zone size being equal to 20 grams of molten silicon.

Evaporation of zinc and thallium dope was so severe that RF arcing made float-zoning impossible. Thallium was tried by diffusion techniques. However, the results were not promising. Thallium has an acceptor level at 0.26 ev above the valence band, and we attempted to activate this level by diffusing thallium into 50-80 N-type silicon at 1200°C. As shown in Graph 1, a plot of log ρ versus 1/T is not linear over the temperature range -85° to 200°C. Furthermore, the thermistors cut from the same diffused silicon wafer were not reproducible as far as their temperature-resistance behavior was concerned. For these reasons, thallium was discarded as a possible silicon thermistor dope.

Iron, manganese, and platinum resulted in polycrystalline float-zone rods even when added at very low concentrations in the float-zone leveling process. Gold, silver, copper, and nickel were added until polycrystallinity occurred during float-zone leveling. With gold, this corresponds to about 0.15 grams per zone; silver, 0.15 grams; copper, 0.2 grams; and nickel, 0.06 grams. Silver and nickel were used as dopants in high-resistivity (greater than 100 ohm cm) N-type silicon, and medium resistivity (35 ohms cm) P-type. The log ρ versus I/T plots of these elements as shown in Graphs 2 and 3 were not linear nor reproducible from one sample to another. Copper, which has a donor level 0.23 ev above the valence band, was also tried by diffusion techniques. Copper was diffused into a 3mm silicon wafer for 24 hours at 1200°C. The log ρ versus 1/T plot of float-zone leveled Cu is shown in Graph 4. There is an undesirable deviation from linearity. The diffusion results were even more erratic.

Gold-Doping of Silicon

Of the elements tried, gold in both P- and N-type silicon produced products which appeared most suitable for thermistor use in the -85° to +200°C range. Gold was first added to 40-60 ohm cm N-type silicon. The resulting silicon had a resistivity of about 130,000 ohm cms at 25°C. This resistivity was dependent on the phosphorus level. When the log of the resistivity of the gold-doped N-type silicon is plotted versus 1/T as in Graph 5, a straight line results over the range of -85° to 200°C with an activation energy measured from the slope of 0.54 ev. This slope corresponds to the gold acceptor level located 0.54 ev below the conduction band.[9] Sufficient gold must be present to overcompensate the N-type impurities rendering them inactive electrically and to provide additional levels for the 0.54 ev conduction. In the particular case noted $\sim$ 21 ppb of gold were added to a bar containing approximately 1.5 ppb of excess N-type carriers.

The effect of the gold level relative to the excess N-type carriers

MODEL #606   DATE 12/14/61

GRAPH NO. 11

THALLIUM DOPED SILICON

RESISTIVITY $\times 10^{-9}$ (OHM CM)

$\frac{1}{°C + 273}$

GRAPH NO. 2

SILVER DOPED SILICON

FLOAT ZONE LEVELED
.05 g (Ag) PER ZONE (±20%)
IN 25-400 N TYPE SILICON

GRAPH No. 3

NICKEL DOPED SILICON

FLOAT ZONE .L-105-20
.0549 NI PER ZONE (~20g)
IN 35÷70 P TYPE SILICON

RESISTIVITY (OHM CM)

$\frac{1}{°C + 273}$

GRAPH No. 4

RESISTIVITY (OHM CM)

1000000

100000

10000

1000

FLOAT ZONE LEVELED
LESS 6K PER ZONE
IN 100M OHM CM N TYPE
SILICON

100

10

1

-85°C -75°C   -40°C   0°C 25°C 65°C   125°C   200°C

$$\frac{1}{°C + 273}$$

RESISTIVITY × 10⁻¹ (OHM CM)

GRAPH No. 5

ΔE = .53 EV.

FLOAT ZONE LEVELED
~ 21 ppb Au in 10-17 OHM CM
N TYPE SILICON

GOLD DOPED SILICON

$$\frac{1}{°C + 273}$$

-85°C   -70°C   -40°C   0°C   25°C   65°C   125°C   200°C

in the starting silicon is shown in Graph 6. The three samples plotted
were cut from a pulled crystal in which the gold level was nearly
critical. That is, the ppb of gold were approximately equal to the
ppb of excess phosphorus at the head of the crystal. Since the gold
(distribution coefficient $\sim 3 \times 10^{-5}$) concentration increases more
rapidly than phosphorus (distribution coefficient 0.35) the relative
gold concentration at 40% of the pulled crystal is larger than at
10%. Notice that the degree of linearity increases from 10 to 30%
and at 40% there is linearity. This is the point at which the gold
is in slight excess over the phosphorus.

Annealing experiments have further demonstrated the criticality
of the gold level. Samples were annealed in argon at 300, 500, and
900°C for 48 hours. The samples had been cut from silicon which
contained gold in excess over the N-type impurities. The silicon
had been prepared by float-zone leveling. As shown in Graph 7,
little change was noted in the temperature-resistance behavior of
samples annealed at 300 and 500°C; the samples annealed at 700° and
900°C began to lose linearity, however. At these temperatures, some
of the gold is probably migrating to dislocations or other imperfections,
reacting with them, becoming electrically inactive and resulting in a
sub-critical gold level and non-linear temperature-resistance behavior.

In fabricating a precise thermistor from the gold-doped N-type
silicon described, some difficulties were encountered. Most electronic
devices, such as radiosondes, will not tolerate resistances above
several megohms because of the parallel conduction of the chassis,
insulators, and moisture. With the material described, if the resistance
at the lowest temperature, -85°C, was about one megohm, the 25°C resistance
of such a unit would be about 100 ohms. Since L/A for such a device would
be about 10^{-3} cm^{-1}, even if the silicon were cut and lapped to the thinnest
wafers possible (say 6-8 mils thick) the area of such a device would be
completely unreasonable, being on the order of 20 cm^2. Therefore,
material with such a high resistivity would not make a convenient low-
temperature thermistor purely from geometry considerations. However,
on the upper end of the temperature range, such material could make
a very suitable thermistor and the log ρ versus 1/T behavior is
nearly linear all the way to 200°C.

Another factor to be considered with gold-doped N-type silicon
is the temperature sensitivity. The gold-doped N-type silicon described
is very sensitive, exhibiting a temperature coefficient of resistivity
of about -7.1% per degree at 25°C. In a radiosonde, the electronic
circuitry will tolerate a resistance change of about three decades
over the -85° to +30°C range. For this purpose, the 0.54 ev thermistor
is too sensitive, exhibiting about five decades of change in the same
region. For some applications, it is therefore desirable to have a
thermistor material which has a lower activation energy and a lower
resistivity.

GRAPHING 6

GOLD DOPED SILICON

GRAPH No.7

ANNEALING OF
GOLD DOPED SILICON
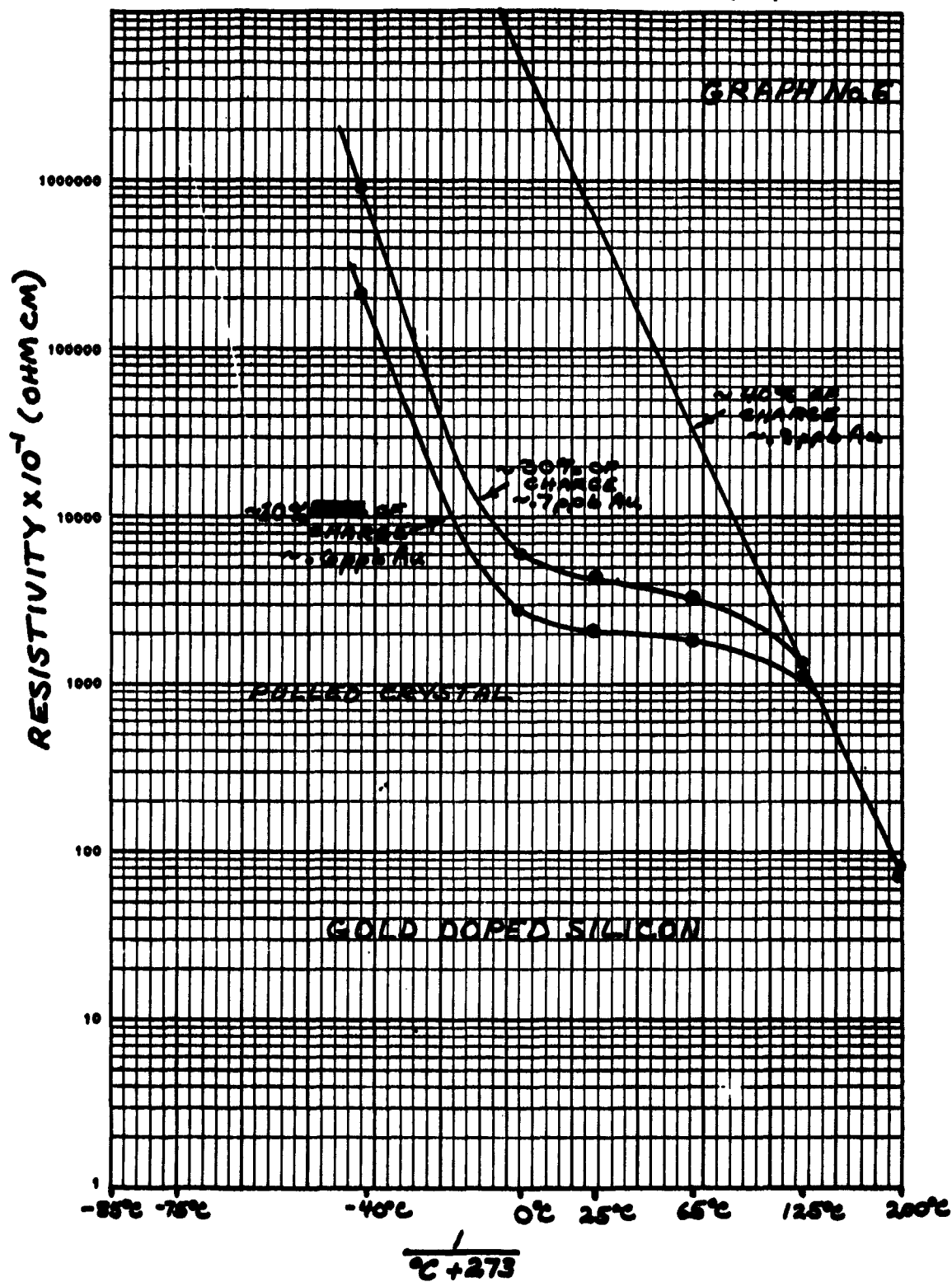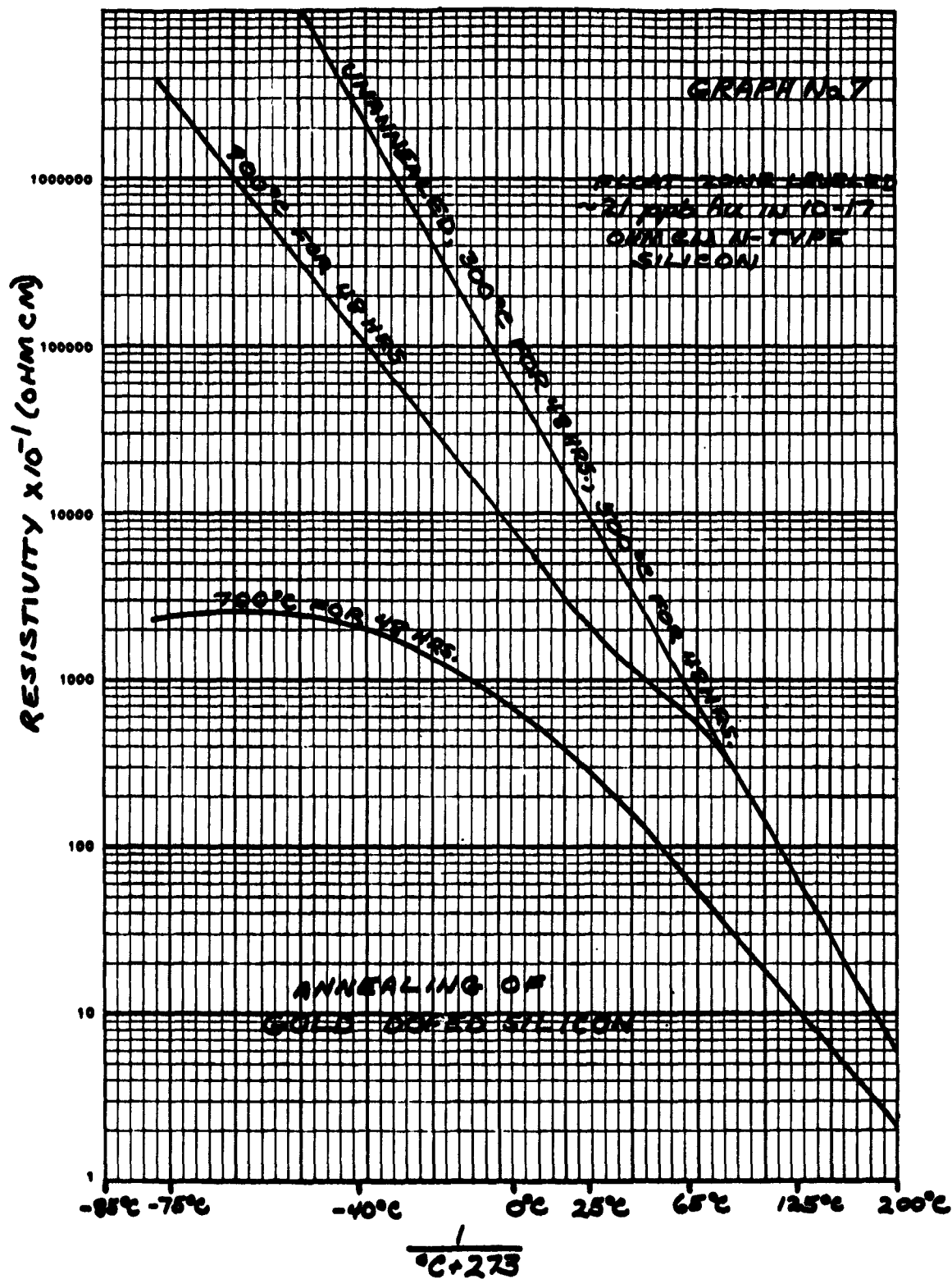
With this in mind, we tried to activate the 0.34 ev donor level of gold in silicon. The 0.34 ev level was activated by gold doping P-type silicon. This doping was accomplished by both float-zone leveling and diffusion techniques. When diffusing, single-crystal silicon wafers approximately 6mm thick are plated or dusted with gold and diffused in an argon ambient at 1200°C for 24 hours. The gold first melts into the surface of the silicon, causing an etched-like appearance and then diffuses throughout. About 1000 ppb of gold can be added by this technique according to the literature (10). By zone leveling techniques, about 30 ppb of gold is the maximum that can be added before polycrystallinity occurs. We feel that this difference is due to the fact that zone leveling results primarily in substitutional gold, whereas diffusion results in substitutional gold as well as gold which migrates to crystalline imperfections. Graph 8 is a typical plot of log ρ versus 1/T for a P-type bar doped with gold by float-zone leveling techniques. Notice that the resistivity is about 400 ohm cm at 25°C. This is considerably lower than that obtained in the gold-doped N-type silicon case. Also, notice that there is some deviation from linearity at higher temperatures; there is essentially linearity between +30°C and -85°C, however. This is the practical working range of a radiosonde.

The resistivity of the gold-doped P-type silicon appears to be a function of the excess boron content, as indicated in Table 2 below:

<p style="text-align:center">TABLE 2</p>

P-Type Resistivity Before Doping at 25°C (ohm cm)	P-Type Resistivity After Doping at 25°C (ohm cm)
0.33 - 0.47	7.5
1.1 - 1.6	23.1
9.2	40.7
50 - 66	80.6

All samples were dusted or plated with gold and diffused in argon at 1200°C, for 24 hours. This relationship was significant because we had a technique for controlling resistivities so that a desirable L/A could be obtained for a device. This material undergoes about three decades of resistance change over the radiosonde temperature range.

In P-type silicon, the product obtained by diffusion is lower in resistivity than the product obtained by float-zone leveling. For example, a 50-66 ohm cm P-type silicon bar, when diffused with gold, has a resistivity of about 80.6 ohm cm at 25°C, while the float-zone leveled product has a resistivity of 400 ohm cm at 25°C. Since more gold is added by the diffusion technique, it is felt that the resistivity of gold-doped P-type silicon is also a function of the amount of gold present.

GRAPH No. 3

ΔE=.32 E.V.

RESISTIVITY (OHM CM)

1000000

100000

10000

1000

100

10

1

FLOAT ZONE LEVELED
~31 epi Au IN 15-20P
TYPE SILICON

-85°C -75°C   -40°C   0°C 25°C   65°C   125°C 200°C

$$\frac{1}{°C+273}$$
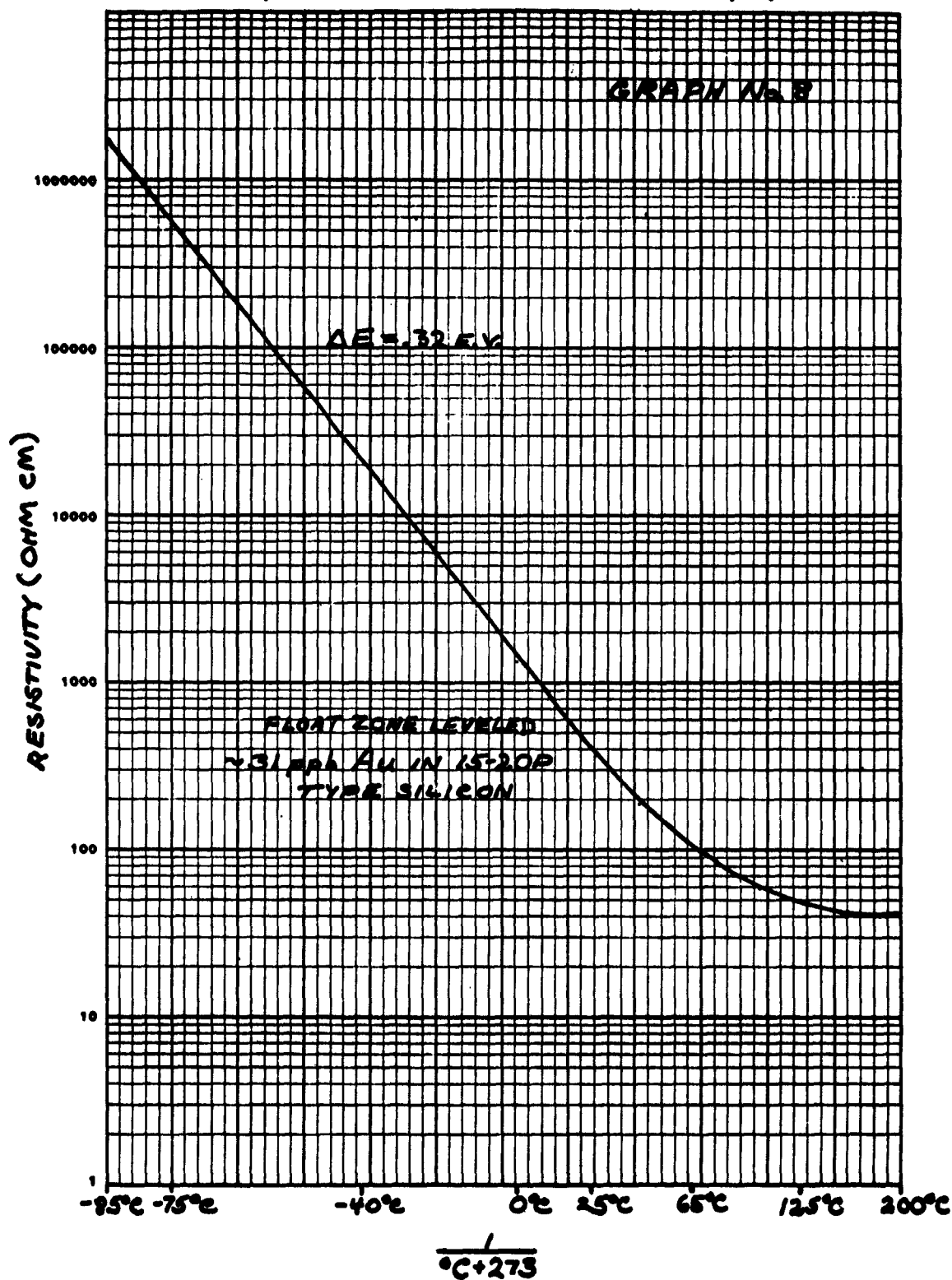
Another interesting phenomenon is the apparent decrease in activation energy or thermal sensitivity as the boron content of gold-diffused silicon is increased. Table 3 below gives activation energies of diffused silicon at various levels of excess boron:

<div align="center">TABLE 3</div>

P-Type Resistivity Before Doping at 25°C (ohm cm)	Activation Energy ΔE of Linear Portion By Least Squares (electron volts, ev)
0.33 - 0.47	0.22
1.1 - 1.6	0.24
9.2	0.26
50 - 66	0.33

Notice that the activation energy drops off to approximately 0.22 ev as the resistivity of the starting boron-doped silicon decreases to 0.4 ohm cms.

Statistical Study

At this point, we felt that the feasibility of using specially doped silicon as a thermistor material had been demonstrated. By varying the silicon type and the amount of gold dope, a series of thermistor materials with suitable activation energies and resistivities should be obtainable. As mentioned previously, doping can be accomplished either by diffusion or float-zone leveling techniques. A statistical study was begun to determine the variabilities to be expected in making devices by the diffusion of float-zone leveling techniques. The decision to make thermistors by diffusion or zone leveling was based on this study.

The float-zone leveled samples in this comparison were prepared by float-zone leveling a 7/8-1", 15 to 20 ohm cm P-type rod with 0.15 grams of high-purity gold. The rod was cut into 12 wafers approximately 5 millimeters thick. After hand lapping with 180 grit SiC paper, they were nickel plated on both sides by the electrodeless technique. Each wafer was cut into twelve 4mm x 4mm x 5mm thermistors. The wafers were numbered alphabetically and the thermistors within a wafer were numbered numerically. Copper leads were soldered to the thermistors with tin, and resistances were measured over the temperature range of -75° to 30°C. Eight rather evenly spaced measuring points were used over this temperature interval. Resistivities were calculated from the resistance readings at various temperatures and the physical size of the thermistors as measured by a vernier caliper.

The first step in preparing the diffusion samples was cutting a 15 to 20 ohm cm P-type rod into 12 wafers approximately 6 millimeters thick.

These wafers were plated with gold on both sides and diffused at 1200°C for 48 hours. The gold-etched surface of these wafers was lapped away so that the final thickness of the wafer was approximately 5 millimeters. The wafers were nickel plated by the electrodeless technique and each was then cut into 12 thermistors as described previously. Again the wafers were numbered alphabetically and the thermistors within a wafer were numbered numerically. Copper leads were soldered to the thermistors with tin, and the resistances were measured as in the float-zone leveled case.

The resistance vs. temperature data were then fed into a Bendix G-15 Computer which computed the least square lines through the points as well as the resistivity profiles along these computed lines. Since in the case of gold-doped P-type silicon there is some deviation from linearity of a log resistivity vs. 1/T plot at temperatures above $\sim$ 30°C, only the points from +30 to -75°C were analyzed.

Standard deviations, σ's, were calculated by variance analysis for ΔE and resistivities at 25°C. A summary of the results of this analysis is given in the table.

TABLE 4

Standard Deviations (σ)

	Diffusion		Float-Zone Leveling	
	ΔE (ev)	Resistivity at 25°C (% Average Reading)	ΔE (ev)	Resistivity at 25°C (% Average Reading)
Uniformity of devices within a wafer	0.011	11.5%	0.004	11.6%
Uniformity of devices from wafer to wafer along a rod	0.019	12.0%	0.005	11.0%

The standard deviations for resistivity of device to device and wafer to wafer along a rod are the same order of magnitude by both doping processes. However, the corresponding activation energy deviations are considerably better in the case of float-zone leveled material. This parameter is independent of physical size but the resistance is not. It was felt that some of the inability to control resistance was due to variation of physical size. The devices had been fabricated as cut on a precision diamond saw. A 2% error in dimensions could result in a 6% error in resistivity. Precision lapping could help reduce this error. The slope of a thermistor must be controlled very accurately to meet the requirements of the contract. The statistical data indicated that the float-zone leveling process produces the least variable product.

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Improvements in Measuring Technique

Resistance measurements were improved by use of the comparison method or ratio technique. An unknown thermistor and a standard thermistor are mounted in opposing arms of a Wheatstone bridge:

$$\frac{R_{UNK}}{R_{STD}} = \frac{R_A}{R_B}$$
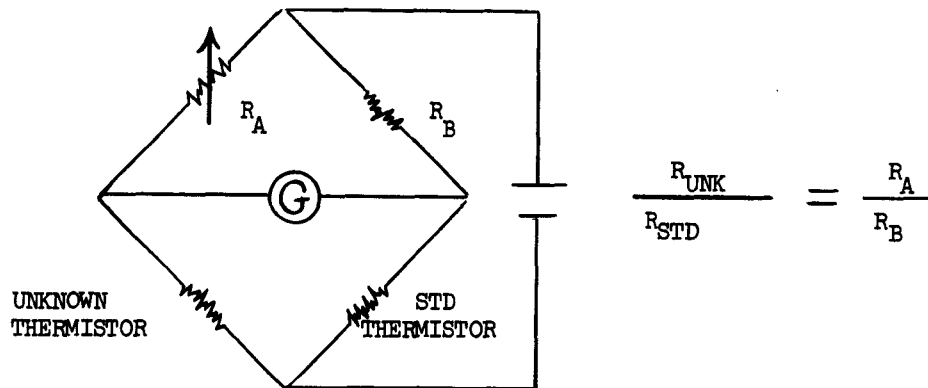
FIGURE 1

Both thermistors are immersed in the same measuring bath. The reading obtained is a ratio of the resistance of the unknown to the standard resistance. Standards are usually chosen so that the ratio will be approximately equal to one. The time constants of the thermistors are small compared to the time of temperature cycling of the bath. The effects due to temperature fluctuation in the measurements baths tend to be eliminated, since these do not appreciably affect the ratio at a given temperature. This technique improved our measurement precision considerably. A statistical study was completed comparing standard deviations of material measured by ratio technique and by direct Wheatstone bridge resistance measurement.

TABLE 5

Standard Deviations (σ)

	Conventional Wheatstone Bridge Resistance Readings		Ratio Technique Using Wheatstone Bridge	
	ΔE (ev)	Resistivity at 25°C (% Average Reading)	ΔE (ev)	Resistivity at 25°C (% Average Reading)
Uniformity of devices within a wafer	0.0041	1.2%	0.0017	1.6%
Uniformity of devices from wafer to wafer along a rod	0.0046	1.1%	0.0019	0.8%
Average value	0.3621	433	0.3648	436

The material measured by the ratio technique shows a significant improvement in activation energy deviations. Resistance deviations are about the same. The deviations represent a considerable improvement over those obtained by direct readings.

The ratio-measuring technique is very important as far as test measuring of the pilot line samples is concerned. There are many samples to be checked at various temperatures. Since all of the thermistors from a given run are to be uniform in resistance within ±2%, the production thermistors should be compared with a standard thermistor of the proper resistance at the various testing temperatures. Samples showing ratios below 0.98 or above 1.02 should be rejected. The variation in temperature of our baths at a given temperature level is on the order of ±0.01 to 0.001°C. The ratio technique tends to eliminate this variation and enables us to measure ratios without deviations that would be experienced if using a Wheatstone bridge and measuring resistance directly.

This technique was also useful in measuring samples during size adjustment which will be discussed later.

4. Contact Problems

During the course of the early work there were indications that
the nickel-silicon contact being used in the experimental thermistors
was causing some non-uniformity in the finished devices. Several
factors led to this belief. The standard deviations for reproducibility
of repeated measurements on a thermistor were often equal to, or greater
than, the deviations for devices within a wafer or from wafer to wafer
along a rod. As the length of a thermistor was decreased, the resistance
was much higher than predicted by a low resistance contact. There seemed
to be a dependence of the resistance ratio or resistance on the amount of
current or voltage applied to a thermistor while being measured. We
decided to make a systematic study of the contact problem and to
consider other contact materials.

Two thermistors were measured by the ratio technique previously
described. An ammeter was mounted in the measuring circuit as shown:

AMMETER

R_A R_B

G

UNKNOWN
THERMISTOR

STANDARD
THERMISTOR
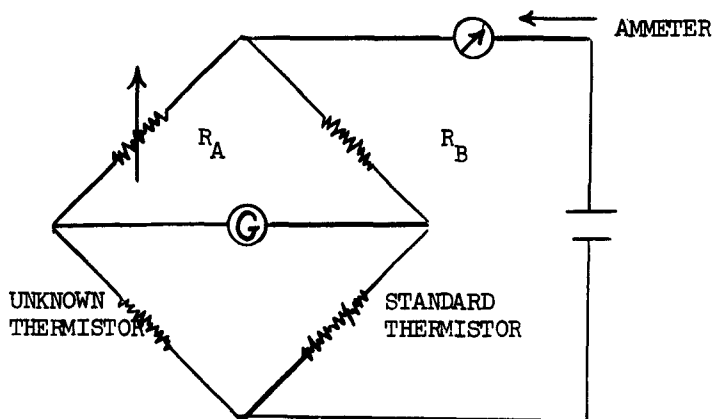
FIGURE 2

The amount of current flowing through the thermistor while not
equal to the current registered on the ammeter is proportional to it.
Graph 9 demonstrates the behavior of the resistivity ratio as the
current in the circuit is increased. The two curves are a result of
reversing the two thermistors in the ratio arms. Notice that ratio
variations on the order of 8% can result by varying the current through
the thermistors. These results are not believed to be due to the
heating effect. The heat effect is the build-up of a temperature
gradient in a heat-producing medium due to the inability of a system
to dissipate heat rapidly. It is inversely proportional to the
coefficient of thermal conductivity. This problem is discussed in the
literature[11]. In the present case the power produced in a thermistor
under normal measuring conditions is on the order of a millimicro-watts.

GRAPH 9

RESISTANCE RATIO vs CURRENT

TEMP = 0°C

$\frac{Th1}{Th2}$

$\frac{Th2}{Th1}$

RESISTANCE RATIO

TOTAL MICRO AMPS IN CIRCUIT

- 21 -
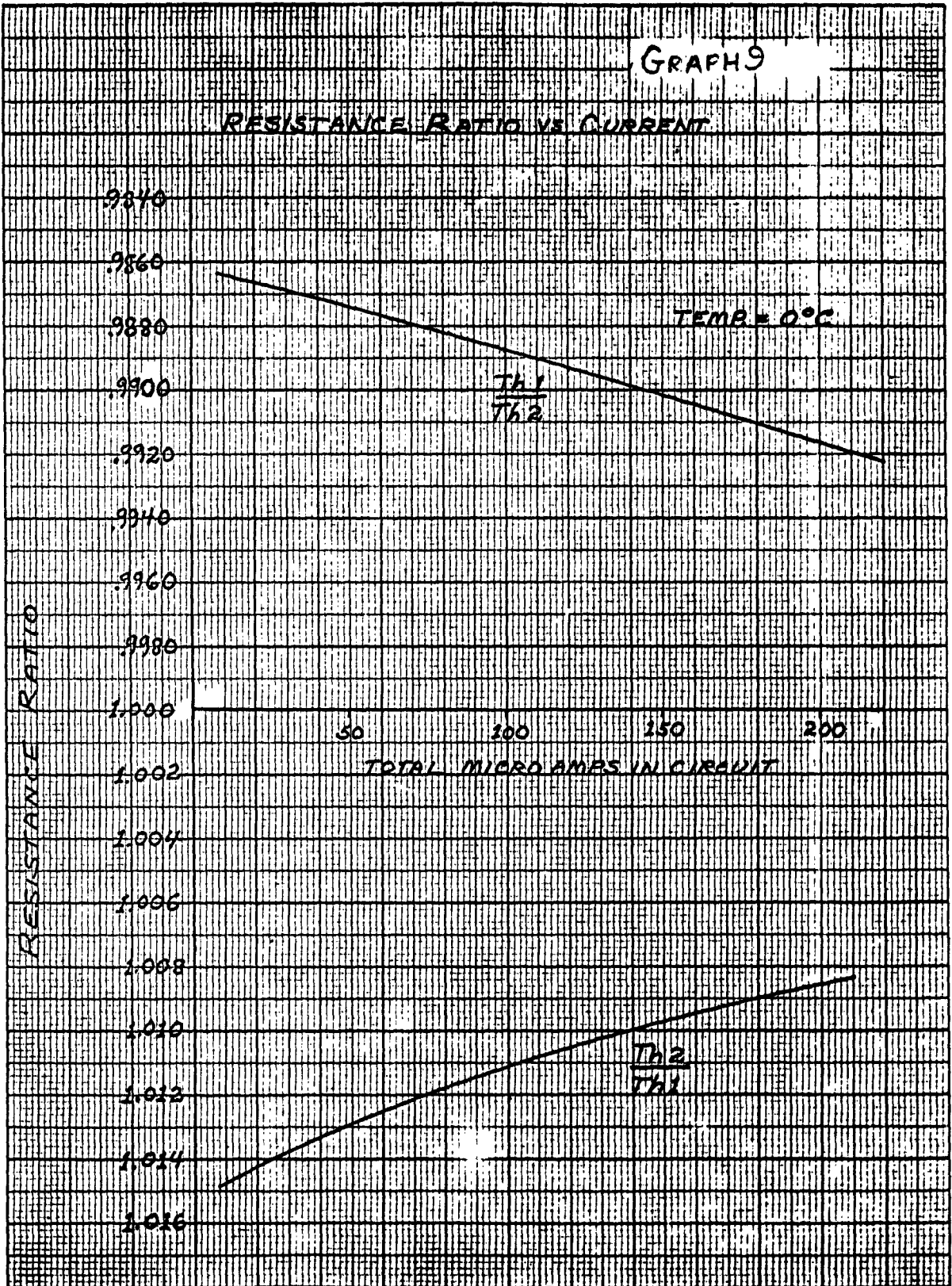
The temperature change to be expected from such heat production is on the order of 10-5°C, if the system were allowed to come to equilibrium. Such a temperature change would not cause a significant decrease in resistivity. It would take a change of 0.44°C at 25°C to result in a 2% error in resistivity. Besides, the standard thermistor would be varying in temperature along with the unknown thermistor, thus minimizing any decreases in resistance due to heating.

Further examples of the resistance behavior of nickel contacts to gold-doped silicon are demonstrated in Graphs 10 and 11. Both measurements were made on the same thermistor at 0°C and -35°C. The resistances were read directly on a standard Wheatstone bridge with the current through the bridge varying as shown on the ordinate of the graphs. Notice that as the current increases from 0, the resistance of the device increases, reaches a peak, and then steadily decreases. The dashed curves are the result of depressing the galvanometer key for an extended period of time and show the result of the heat effect especially at higher currents. It is interesting to note that the peak of the curve shifts toward the left as the temperature is decreased. In fact, at -75°C there is often no peak at all, but a steady decline of the resistivity as a function of the current.

It was obvious that the nature of the nickel to gold-doped silicon contact would have to be studied further. A 4 x 4 x 5mm gold-doped thermistor was set up for potentiometric measurement as shown in Figure 3.

FIGURE 3

Not to Scale

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GRAPH 10

RESISTANCE VS CURRENT

RESISTANCE X 10⁻² — OHMS

MILLIAMPERES

GRAPH 11

RESISTANCE VS CURRENT

MILLIAMPERES

RESISTANCE X10³ OHMS
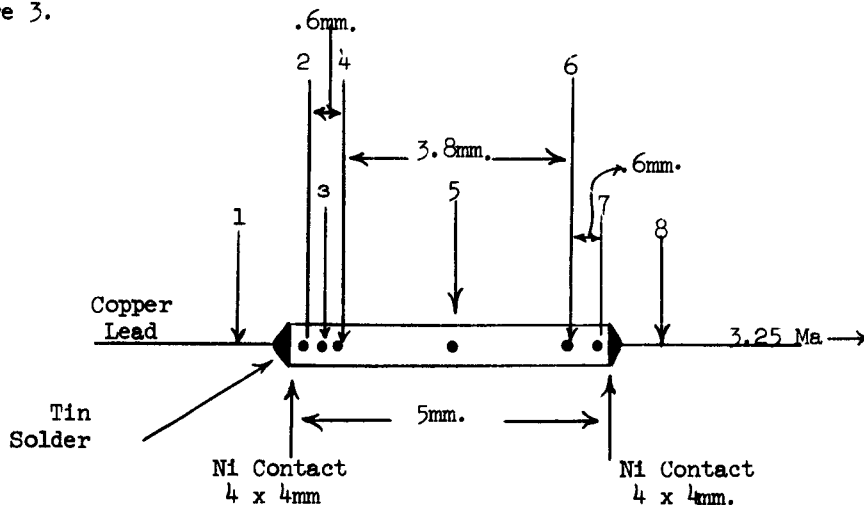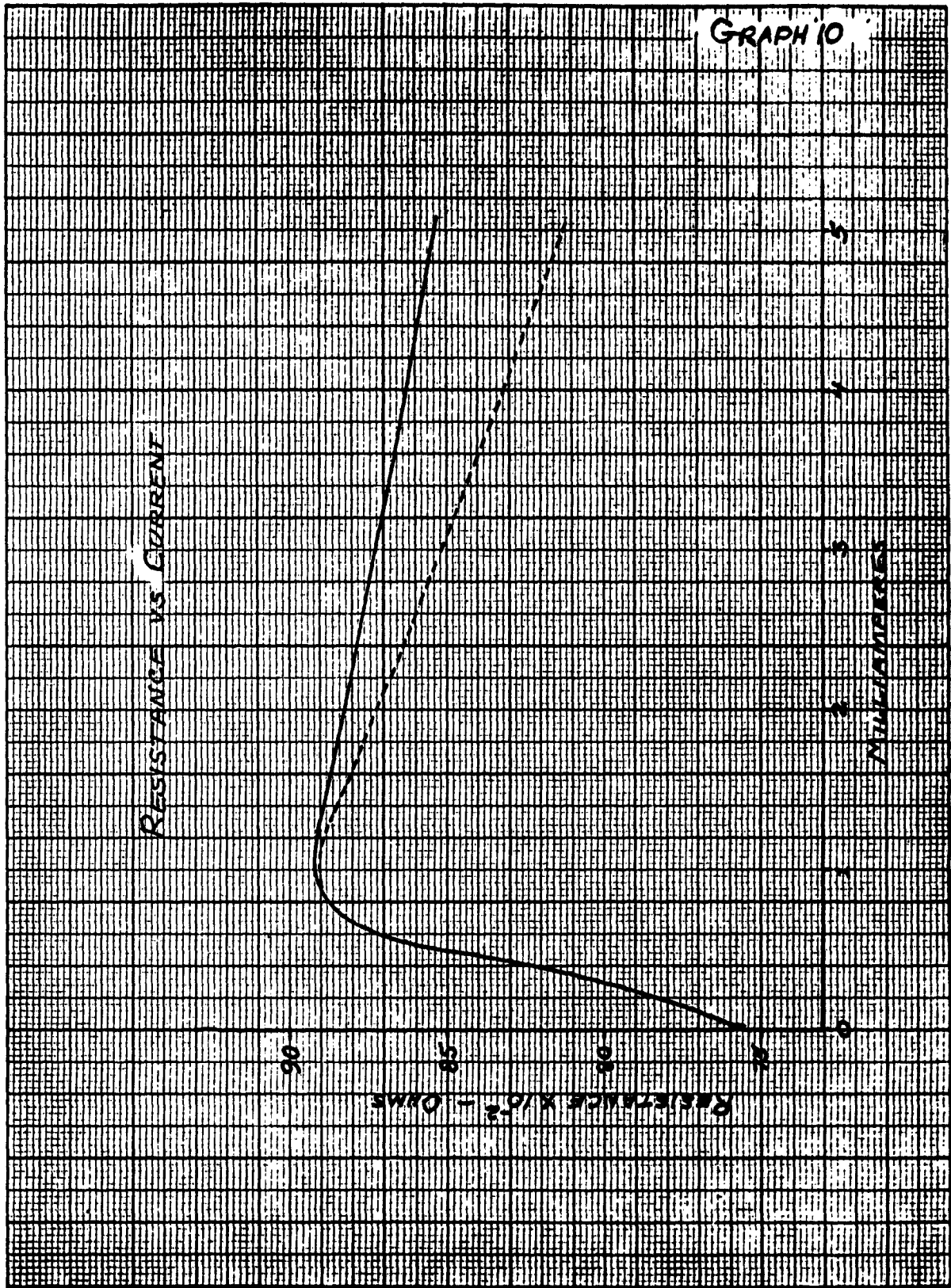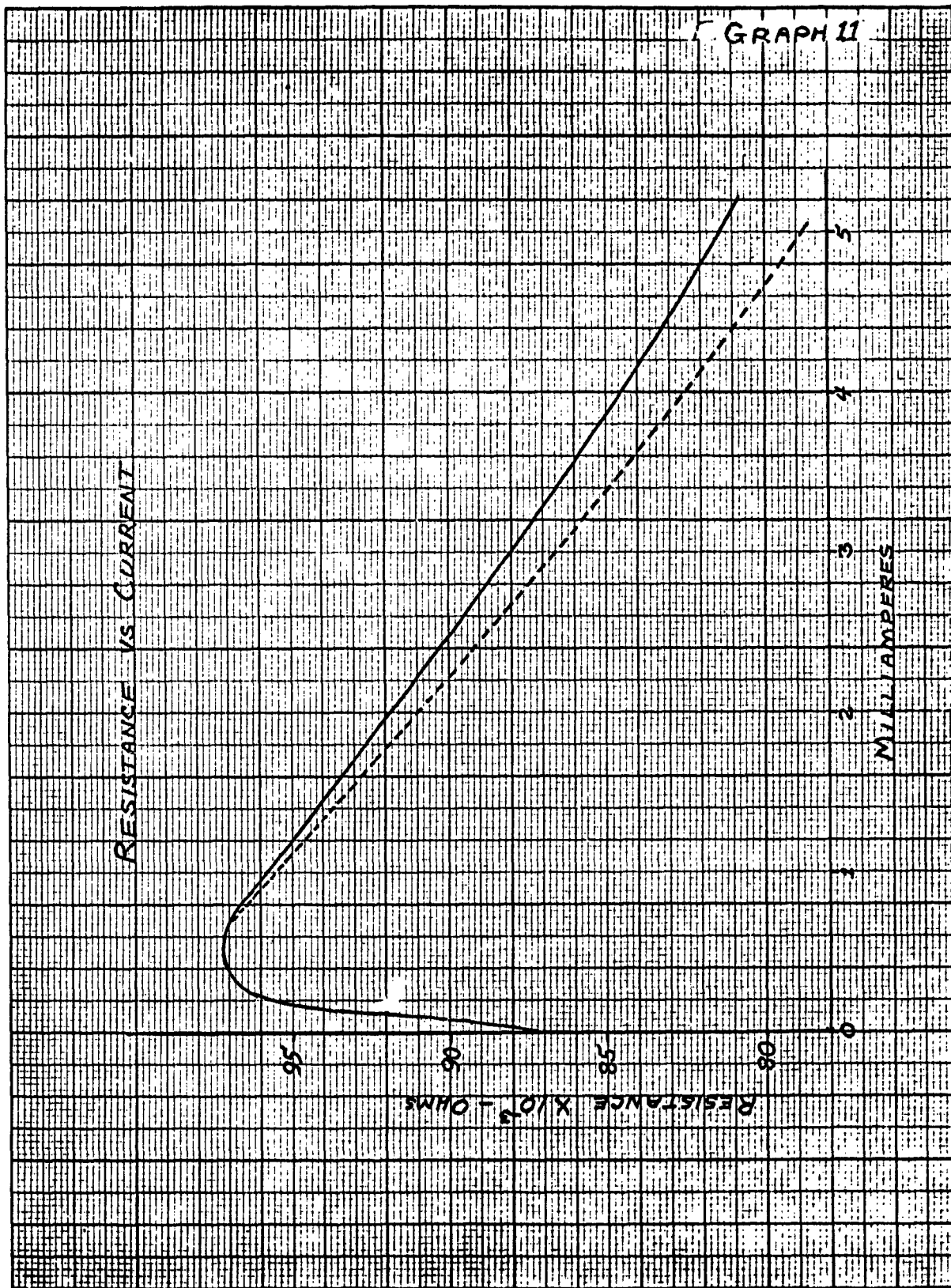
TABLE 6

REFERENCE POINTS	RESISTANCE READINGS (OHMS)
1-8	1072
1-5	524
1-3	257
1-2	207
1-7	911
5-8	560
4-6	532

Potentiometric measurements eliminate the effect of current since the current flow through the petentiometer probes is 0. Voltage readings were made between various points on the thermistor as indicated in the diagram.

Results of the measurement from points 1 to 8 indicated that the total resistance of the element is 1,072 ohms. The measurement between points 1 and 2 indicated the contact resistance is on the order of 200 ohms. By comparing measurements between points 1 and 2 and points 1 and 7, it was seen that the resistance of the gold-doped thermistor element was approximately 700 ohms. We had a case in which 400 ohm cms of a total element resistance of 1072 ohm cms is accounted for by contact resistance. This was much too great and could have had serious consequences, especially on thinner elements.

Another series of experiments had indicated that the nickel to gold-doped silicon contact varied with temperature in a manner similar to gold-doped P-type silicon. This usually occurred when the resistivity of the silicon to which the plating was attached was high. Graph 12 shows the effect of plating ordinary P-type silicon of various resistivities with nickel and subsequently measuring the total resistance of the element. In this case, the silicon slugs measured 4 x 4mm in size. In the P-type case when the resistance is high enough (excess impurity concentration is low) a linear $\log \rho$ vs. $1/T$ behavior similar to that of gold-doped silicon occurs from about -75 to 0°C.

This behavior might have two explanations. It may be due to the diffusion of nickel during the plating and soldering process into the silicon immediately adjacent to the contact. This nickel could introduce energy levels with conduction properties similar to those introduced by gold. In the high P-type case, the chances of the nickel controlling the conduction picture are greater and the phenomenon will manifest itself more easily.

Another possible explanation of this phenomenon may be the establishment of a surface barrier potential when the nickel is plated onto the gold-doped P-type silicon. This generally occurs because the Fermi level of the

GRAPH 12

RESISTANCE - OHMS X10

1000000

100000

10000

100. OHM CM. P-TYPE

1000

1.1 OHM CM. N-TYPE

0.1 OHM CM. N-TYPE

100

0.5 OHM CM. N-TYPE

0.5 OHM CM. P-TYPE

10

1

-85°C -75°C -60°C   -30°C   0°C 25°C 65°C   125°C 200°C

$$\frac{1}{°C + 273}$$

- 26 -
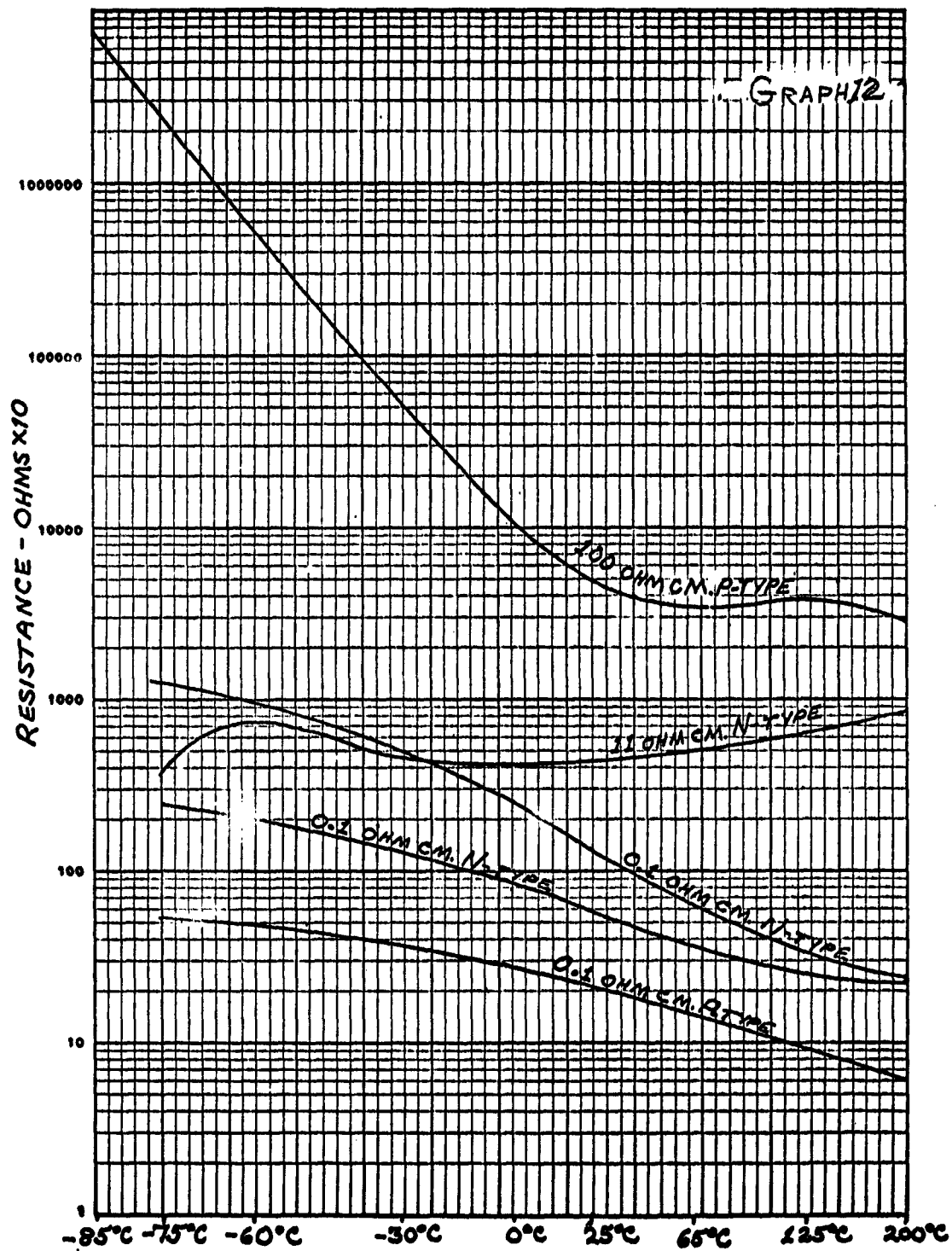
semiconductor is higher than the Fermi level in the metal. When contact is made, the electrons flow from the semiconductor to the metal since they are at a higher potential energy. This leaves the semiconductor with a net positive charge which attracts the electrons in the metal to the contact. The positive electrostatic charges in semiconductor are attracted toward the contact so that a contact barrier potential occurs. This contact is usually rectifying and essentially non-ohmic. It is influenced by carrier injection and applied voltage. Technique of preparation of the contact can often have a great deal to do with the rectifying or ohmic behavior of a contact. (12) Frequently, contacts can be made more ohmic by merely roughing or damaging the surface before the application of the plating. Needless to say, the behavior of such contacts is unpredictable.

Contacts on Gold-Doped P-type Silicon

At this point, we decided to try producing contacts of aluminum on the gold-doped P-type silicon. Aluminum is a P-type dopant, hence if it is plated on the surface of P-type silicon and alloyed into that surface there should be a gradation from metallic conduction to strong P^+ to the P level of the bulk of the semiconductor. The presence of the strong P^+ -type area between the metal and the semiconductor proper prevents the injection of carriers when the junction is biased. There in not a barrier preventing the flow of charges from the semiconductor to the metal. Such a contact is essentially ohmic for all intensive purposes. Furthermore the resistance of such a contact should be small compared to the resistance of the gold-doped silicon. It should have little effect upon the total resistance of a thermistor unit.

Several contacts of aluminum were made to both ordinary P-type silicon and gold-doped P-type silicon. These contacts were studied to see if they were ohmic and suitable for use in thermistors. After many difficulties a research process was worked out for making aluminum to silicon contacts.

In preparing the silicon wafers for aluminum deposition, they are cut on a precision diamond saw and hand lapped with 180 grit silicon carbide paper. Roughness of the lapped surface is important, since fine grit and smooth lapping can result in poor adhesion between the aluminum and silicon surfaces. After lapping, the silicon is washed with D.I. water, wiped with acetone, washed with alcohol, and blown dry with air. It is very important that no dust gather on the silicon since any dust particle will result in an area of poor deposition on the final wafer.

A small quantity of reagent-grade aluminum turnings is placed in a crucible of densified graphite approximately 1cm in diameter. This crucible is placed in the bottom of a 2 x 2 inch round bottom quartz crucible. A holder for the silicon wafer is mounted at the top of the crucible in notches cut for that purpose. (See Figure 4). A second crucible is inverted over the entire assembly and is placed on an RF coil of a Kinney vacuum float-zone refiner. When the vacuum in the Kinney reaches approximately 0.2×10^{-4}mm Hg the RF power is turned on and warming of the densified graphite crucible is begun. In our

case, power is maintained on the 10 kw, 2-5 megacycle RF generator
at approximately 35% of full on the variac control. The aluminum
melts and begins to evaporate inside the crucibles. Initially one
can see the heat glow of the graphite crucible and the silicon wafer
above it. When you can no longer see the crucible or silicon wafer
the aluminum deposition is complete and the heat is turned off. The
system is allowed to cool. Too much heat applied too rapidly can

ALUMINUM DEPOSITION APPARATUS

2 x 2" Quartz
Crucible

Adjusting
Screws

S.S.
Ring

Si
Wafer

Silicon Wafer
Holder

Notches

2 x 2" Quartz
Crucible

Top View

Aluminum

Densified
Graphite
Crucible

RF Coil

Side View
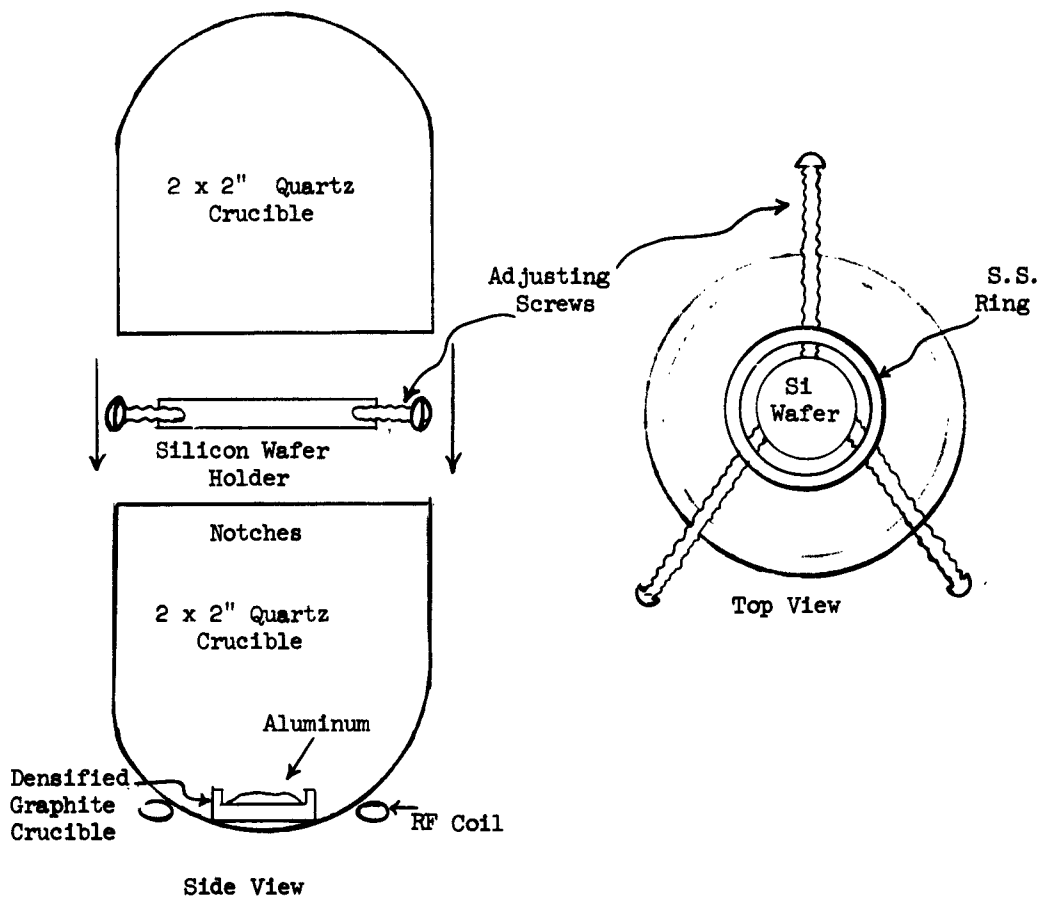
FIGURE 4

Approximately to Scale

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result in a flash evaporation and a poorly deposited aluminum surface. It is desirable not to have a thick aluminum deposition.

After cooling, the wafer is taken from the vacuum chamber and handled very carefully. In this condition the aluminum plating is easily marred or damaged. We have found that a uniform white silver deposition is indicative of a good aluminum plating. A brownish-looking surface indicates that not enough aluminum has been evaporated, or that too much power was applied, so that aluminum has already alloyed into the silicone surface.

The next step is alloying the aluminum into the silicon surface creating the high P^+ area. This is accomplished by heating the wafer under a helium ambient for 20 minutes at 580-630°C as read on a thermocouple mounted in a quartz tube near the wafer. After 20 minutes, the wafer is pulled to the end of the furnace and allowed to cool under the helium flow for a period of about 20 minutes. This is done to avoid oxidation of the aluminum surface at elevated temperatures. When the silicon wafer is taken from the furnace the alloyed surfaces should not be touched. A brownish-looking surface indicates that alloying has occurred. A white-silver appearance indicates that there has been no (or poor) alloying and the bond will probably be poor.

The next step is to nickel-plate the aluminum-alloyed surface by the electrodeless technique. It is essential to keep this plating thin. Plating aluminum-alloyed silicon by the electrodeless technique is somewhat slower than when plating silicon by the electrodeless technique. This plating can take 5 minutes at 96°C. Usually by the time you can observe nickel being plated on the aluminum surface, there is sufficient nickel-plating.

The wafers can then be cut into parallelopiped-type thermistors using the precision diamond saw, or cylindrical shapes using ultrasonic dicing techniques. Leads are soldered to the nickel-plated aluminum surfaces, using as little heat as possible.

The aluminum silicon contacts were tested for temperature-resistance behavior. First, aluminum contacts on ordinary P-type silicon were tested. Graph 13 shows the results of aluminum contacts to 19 ohm cm P-type silicon and 13 ohm cm P-type silicon. The resistances plotted are the total element resistances. In both cases, the resistances at 25°C can be accounted for solely by the bulk resistivity of the silicon. This means that the contact resistances are very small and negligible. The temperature-resistance curves are characteristic of ordinary P-type silicon.

Comparison was made between an aluminum contact and a similar nickel contact. Potentiometric measurements were made on thermistors made of similar gold-doped P-type silicon. In one case the contacts were aluminum, and in the other case the contacts were nickel. Measurements were made between one lead and a point approximately 1.5 mm from the contact.

GRAPH 13

ALUMINUM CONTACTS ON P-TYPE SILICON

RESISTANCE - OHMS x 10^2

19 OHM CM. P-TYPE @ 25°C

13 OHM CM. P-TYPE @ 25°C

DEVICE SIZE 4X4XI mm.
CONTACT SIZE 4X4 mm.

-85°C -75°C -60°C -35°C 0°C 25°C 65°C 125°C 200°C

$$\frac{1}{°C+273}$$
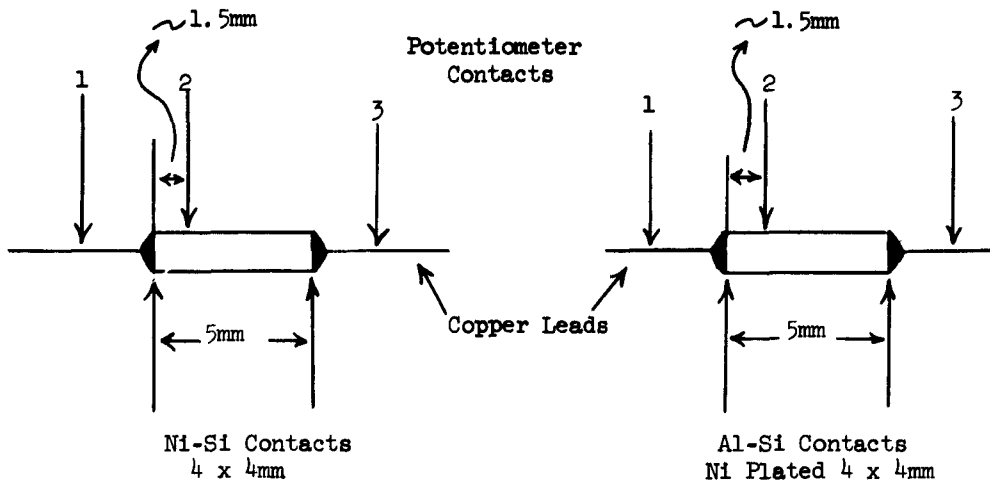
FIGURE 5

Not to Scale

Measurements were also made from lead to lead.

In the case of the aluminum contact, the potentiometric measurement between the lead and interior point (1-2) accounts for approximately 30% of the total resistivity of the element. In the case of the nickel contact, a similar measurement accounts for approximately 40% of the total resistivity of the element. These data indicate several things. First, the aluminum contact resistance is very small and when added to even a smaller section of gold-doped silicon, does not appreciably affect the total resistivity or temperature-resistance behavior. The nickel contact as mentioned previously can account for appreciable portion of the resistance of a thermistor. However, its temperature-resistance behavior is very similar to that of gold-doped silicon. In fact, adding this resistance to the resistance of a portion of gold-doped silicon does not affect the slope of the temperature-resistance curve to any appreciable extent. The nickel P-type silicon contact is undesirable from the standpoint of its behavior under applied voltage as discussed previously. There was little doubt that an alloyed aluminum contact to gold-doped P-type silicon would be very desirable for thermistor applications.

Contacts on Gold-Doped N-Type Silicon

Initially, electrodeless plated nickel was used as a contact for N-type gold-doped thermistors. While nickel is probably a donor and should produce an ohmic contact, the samples showed considerable drift when annealed at 210°C.

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Fearing that the thermistors may have been contaminated while soldering the leads, a solution of nickelous chloride was used instead of the commercially available soldering flux. Annealing and remeasuring the samples gave the following results:

TABLE 7

Sample No.	Flux	0 hrs.	672 hrs.	840 hrs.
1308	Ordinary Paste Flux	97,000	117,600	
1309	"	101,400	114,600	
1310	$NiCl_2$	313,900		303,100
1311	$NiCl_2$	43,940		45,490
1312	$NiCl_2$	247,100		251,500
1313	$NiCl_2$	110,300		114,600

Although there was some improvement in stability it was far from satisfactory.

Gold, gold-antimony alloy and antimony sub-layers were used as a "cushion" between the nickel and the silicon to improve the ohmicity of the contacts. The general technique of applying these materials is to evaporate under vacuum and deposit directly on the silicon wafers. The wafers are then heated, sintered, or alloyed at elevated temperatures. After etching, usually with concentrated HF, the wafers are plated with electrodeless nickel. The wafers are diced and leads are attached before the final check of resistance and annealing at 210°C.

Sub-layers of gold, when applied in the described manner, showed an increase in resistivity after annealing, probably because the gold contact was changing the concentration of gold in the gold-doped silicon.

Sub-layers of gold-antimony alloy were deposited using the Kinney unit. In fact that gold has a much higher melting point than the antimony made the deposition difficult to control. The final deposited alloy on the wafer had a gold concentration that was a function of evaporating time while the amount of antimony was practically constant. The following table gives the results of two typical samples:

TABLE 8

Sample No.	Resistance After - Hrs. at 210°C (ohms)		
	0 hrs.	328 hrs.	852 hrs.
1314	55,920	55,750	Broken Contact
1315	54,520	54,590	55,540

Sub-layers of antimony were deposited on three wafers using the Kinney unit and then alloyed at 500° , 800° and 1200°C. After etching and nickel plating, leads were attached. Results after annealing for various lengths of time at 210°C are given below.

TABLE 9

Resistance After - Hrs. at 210°C

Alloying Temperature	0 hrs.	17 hrs.	37 hrs.	87 hrs.	104 hrs.	222 hrs.
500°C	1662	1675	1698	-	Contact Broken	-
800°C	1735	1760	1798	-	1962	Contact Broken
1200°C	1240	1258	-	1262	--	1264

The sample which was alloyed at 1200°C appears to be stabilizing after an initial 2% change in resistance. The continuous rise in resistance until the contact breaks was typical of weak mechanical contacts due probably to a layer of non-alloyed antimony between the nickel and the antimony-silicon alloy.

The results obtained were encouraging enough, however, to make some more experiments. Below are some of the results obtained by alloying antimony-deposited gold-doped N-type silicon wafers. 0.005g of antimony was deposited per seven wafer sides.

TABLE 10

Resistance After - Hrs at 200°C

Wafer No.	Alloying Temperature	0 hrs.	50 hrs.	194 hrs.	1050 hrs.
4	1200°C	8,981	8,892	8,769	8,841
5	1000°C	10,376	8,889	8,584	8,535
6	1000°C	11,080	9,335	8,953	8,748
7	1000°C	10,934	9,238	8,827	8,653
8	1100°C	13,123	10,505	10,530	10,845
9	1100°C	12,630	12,117	12,214	12,235
10	1200°C	13,130	12,565	12,634	12,630

The lack of uniformity of these three sets of wafers made under the same conditions resulted in a closer examination of the technique of nickel plating N-type silicon. We assumed now that the lack of reproducibility was due to lack of uniformity, contamination or oxidation of the surface of the wafers, or some other fault of the nickel

plating process.

A number of quick tests were performed on every step of the nickel plating process. The results were very interesting. It was found that a greasy fingerprint on the wafer before or after lapping could show as a spot difficult to nickel plate or as a well defined fingerprint after the wafer had been nickel plated. Two degreasing cycles were added to avoid this effect.

It was also noted that two wafers seldom nickel plated in the same way. We reached the conclusion that a strong etch just prior to the nickel plating operation was necessary. Etching the wafer with a mixture of HF and HNO_3 left a too-smooth surface for good nickel adhesion. Concentrated HF gave a fair bond, but not good enough. Sodium hydroxide gave a very good cleaning to the wafer. The small amount left on the wafer increased the chemical activity of the nickel plating solution yielding a nickel deposition so thick that it would peel off. Boiling ammonium hydroxide seemed to clean the surface of the wafer in a gentle and uniform way. Very small bubbles on the surface of the wafer indicate that the wafer is ready for the nickel plating solution.

A strength test for the adhesion of the nickel plated film to the silicon was made soldering leads of 28 or 30 gauge copper wire to 2.2 x 2.2mm thermistors and pulling the wires apart. The 2.2 x 2.2mm contacts were considered to be good only if the wire would break before the contacts did.

While in production two more sets of wafers were found to be defective. The failure was traced in one set to the Teflon-covered forceps used to handle the wafers. The Teflon had peeled off and the exposed metal was reacting with the solutions or the silicon. In the other set, the wafers had been exposed to the atmosphere for a short period prior to nickel plating and the surface was covered with a film of oxide.

For testing the new nickel plating technique we selected two gold-doped silicon crystals: 1177, initially 5 ohm cm N-type; and 3253A, initially 8 ohm cm N-type. Wafers 1.2mm thick were cut and measured:

TABLE 11

Resistance at 25°C
After - Hrs at 200°C (Ohms)

Wafer No.	Contacts	0 hrs.	41 hrs.
1177-W1	Ni-plating only	1502	1501
1177-W2	Ni-plating only	1531	1536
3253A-W1	Ni-plating only	4842	4885
3253A-W2	Ni-plating only	4870	4850

In most cases the changes upon heating are less than 1%. Wafers
3253 A-W1 and 3253A-W2 were cut into 2 x 2mm thermistors. Results
of resistance measurements are given below:

TABLE 12

After - Hrs. at 200°C (Ohms)

Thermistor No.	ᐱ hrs.	17 hrs.
3253A-W1-1	460,000	460,000
W1-2	441,000	447,000
-3	448,000	443,000
-4	448,000	449,000
-5	450,000	450,000
-6	460,000	462,000
3253A-W2-2	457,000	461,000
W2-3	463,000	464,000
-4	452,000	454,000
-5	460,000	462,000
-6	478,000	475,000

The distribution of resistances is rather narrow. This is an
indication of good stability. Changes upon heating are also relatively
small.

Further measurements before and after the thermistors had been
adjusted to 500K showed a continuous downward drift. The problem
was traced to leakage on the edges of the thermistors. It seems
that they were contaminated with some low conductivity material.
(i.e. finger oil).

A good washing of the thermistors with trichloroethylene followed
by acetone and alcohol restored the resistance to the orginal value.
For example: thermistor W2-39 had an orginal resistance of 475K. After
167 hours of annealing, the resistance fell to 450K. At 328 hours the
edges were cleaned and the resistance was up to 473K - practically the
same orginal value.

The case of the adjusted thermistors was similar.

TABLE 13

Sample Number	Measurement Before Cleaning	Measurement After Cleaning
W-1-33	456K	495K
W-1-34	418K	499K
W-1-35	440K	492K
W-1-36	406K	505K

This chart shows clearly the effect of the leakage on the edges of the thermistors and the way to eliminate it. The following formula gives the value of the leakage as a function of the resistance of the thermistor.

$$R_e = R_t \ (100\text{-}e)$$

where:

R_e - is the leakage or resistance of the edge.

R_t - is the resistance of the thermistor.

e - is the value of the drift in percent.

For example:

A thermistor of 500K (R_t) went down to 450K or 10% (e), substituting, we have that R_e = 500L (100 -10) = 500K (90)

$$R_e = 40 \ \text{Meg.}$$

After the nickel plating technique had been improved, we used the experience to prepare four more wafers with antimony sub-layers etching to take off the excess Sb. Ammonium hydroxide was used as an etch just prior to depositing the nickel film. Results of resistance measurements after a number of hours annealing at 200°C were as follows:

TABLE 14

Resistance at 25°C
After - Hrs. at 200°C (Ohms)

Wafer No.	Contacts	0 hrs.	24 hrs.	386 hrs.	457 hrs.
3253A-W3	Sb sublayer alloyed at 850°C for 5 min.	7305	7268	7304	7306
3253A-W4	Sb sublayer alloyed at 850°C for 5 min.	7385	7359	7345	7345
3253A-W5	Sb sublayer alloyed at 1000°C for 5 min.	5655	5649	5688	5690
3253A-W6	Sb sublayer alloyed at 1000°C for 5 min.	5586	5588	5641	5641

It appears that the technique of alloying Sb sub-layers to the silicon wafers can be used to obtain 200°C stability. Also, there is the possibility that the alloying temperature may be used to control the final resistivity of the gold-doped silicon.

At this point after several months of doubtful results, we felt that we had not one, but two solutions to the problem. For production purposes, just nickel plated wafers were used because the technique is simpler and there is no change in resistivity. More experiments would be necessary to find the exact relationship between alloying temperature and final resistivity of the wafer with Sb sub-layers. It was our opinion that either technique could satisfactorily meet the contract requirements, both mechanically and electrically. However, as we previously pointed out, the operators must handle the thermistors with extreme care or contamination with odd effects will follow.

5. Slope and Resistivity Vs. Starting P-Type Resistivity

A study was completed to determine the dependence of slope and resistivity upon P-type resistivity of the starting silicon. All rods used in this study were 7/8-1 in diameter and were float-zone leveled with 0.15 grams of high-purity gold. The results of this study are given in the table.

TABLE 15

Average Starting P-type Resistivity at 25°C (ohm cm)	Average Slope ΔE (ev)	Resistivity after doping at 25°C (ohm cm)
9.5	0.3273	246
19	0.3275	495
22	0.3263	522
25	0.3267	915
45	0.3264	1110

There is no appreciable change in slope, all values falling within .0012 ev. There is a definite increase in resistivity of the thermistor material as the resistivity of the starting silicon is increased. This relationship was useful for production purposes. For instance, the resistance of a unit not only was controllable by size but also by the resistivity of the thermistor material being used.

6. Annealing Experiments

We conducted annealing experiments at elevated temperatures to determine whether the thermistor elements could be stabilized by this technique. The temperature-resistance response of samples was measured after heating for various lengths of time at 210°C and higher temperatures. Data for a typical series are given below.

TABLE 16

Resistance After - Hrs. at 210°C (ohms)

Sample No.	0 hrs.	93 hrs.	189 hrs.	351 hrs.	470 hrs.
1178	305	293	292	289	288
1180	305	284	284	282	280
1182	345	308	305	301	305
1184	287	283	282	282	282

Average Slope After - Hrs. at 210°C (ev)

Sample No.	0 hrs.	93 hrs.	189 hrs.	351 hrs.	470 hrs.
1178	0.3269	0.3257	0.3266	0.3271	0.3266
1180	0.3268	0.3255	0.3258	0.3259	0.3259
1182	0.3283	0.3276	0.3274	0.3277	0.3272
1184	0.3269	0.3268	0.3270	0.3268	0.3264

There does not seem to be any appreciable change in slope. The resistance does tend to level off after several hundred hours at 210°C. Hundred-hour differences here frequently result in less than 1% change in resistance.

A sample such as 1182 is to be viewed with suspicion. The decreasing resistance followed by an increase usually indicates a poor contact that is beginning to separate. Take for example, the following series:

TABLE 17

Resistance After - Hrs. at 210°C (ohms)

Sample No.	0 hrs.	162 hrs.	324 hrs.	464 hrs.
1238	599	412	414	446
1239	627	494	479	599
1240	400	342	321	321
1241	386	332	332	334
1242	612	489	534	C.B.
1243	601	600	621	C.B.

C.B. - Contact Broken

The contacts on these samples were generally poor. In almost every example, the resistance decreases and increases. Contacts actually broke in two cases after 464 hours and in the other cases were separating. The average slopes are not very uniform and frequently are less than the 0.3250 to 0.3280 normally found in most cases for gold-doped P-type silicon. This would be the case if a non-thermally sensitive contact resistance was being added to the resistance of a device.

Some samples show little change upon annealing as in the following series:

TABLE 18

Resistance After - Hrs. at 210°C (ohms)

Sample No.	0 hrs.	95 hrs.	216 hrs.	428 hrs.	738 hrs.
1265	562	561	561	561	558
1266	556	556	557	554	554
1267	547	539	539	538	536
1268	518	514	516	514	516

Average Slope After - Hrs. at 210°C (ev)

Sample No.	0 hrs.	95 hrs.	216 hrs.	428 hrs.	738 hrs.
1265	0.3262	0.3266	0.3270	0.3266	0.3265
1266	0.3263	0.3269	0.3260	0.3268	0.3268
1267	0.3263	0.3265	0.3258	0.3261	0.3256
1268	0.3268	0.3264	0.3249	0.3259	0.3257

After more than 95 hours at 210°C the changes in resistance are less than 1%. Changes in slope are not appreciable. Several other follow-up series also showed good results in stability and uniformity. The following series of thermistors was cut from the same wafer and shows good uniformity and initial thermal stability.

TABLE 19

Sample No.	Resistance After - Hrs. at 210°C (Ohms)		Average Slope After - Hrs at 210°C (ev)	
	0 hrs.	72 hrs.	0 hrs.	72 hrs.
1326	635	635	0.3263	0.3268
1327	604	603	0.3264	0.3270
1328	610	610	0.3259	0.3267
1329	611	612	0.3260	0.3266
1330	631	632	0.3249	0.3258
1331	614	613	0.3255	0.3272
1332	606	605	0.3264	0.3271
1333	610	609	0.3261	0.3270
1334	608	610	0.3261	0.3268
1335	680	704	0.3258	0.3246
1336	610	612	0.3260	0.3273

Only sample 1335 shows evidence of instability. This is indicated by
an increase in resistance after 32 hours and a decrease in slope. The
increase in resistance is indicative of a contact which is beginning
to separate. In P-type silicon the value of the slope itself is
indicative of a good ohmic contact. In samples with stable contacts
the average slope will normally run between 0.3250 and 0.3280 ev. When
the slope of a thermistor falls below these limits, as in the case of
1335, it is to be viewed with suspicion as far as stability is concerned.

The importance of a good contact cannot be overstressed. Frequently
it is the samples which show the greatest decreases in resistance upon
the initial heating that later increase and result in separated contacts.

Annealing experiments were also conducted at higher temperatures.
Leadless samples were annealed at 300°C, 400°C, and 500°C in air and
helium. At 400 and 500°C the contacts become discolored, brittle, and
difficult to solder. They also tend to separate. The following series
was annealed at 300°C and then at 210°C to see if changes would occur
at the lower temperature.

TABLE 20

Resistance After - Hrs at 210°C (ohms)

Sample No.	300°C for 78 hrs (ohms)	145 hrs.	290 hrs.	458 hrs.
1258	1229	1232	1230	1228
1259	1330	1340	1347	1357
1260	1284	1340	1287	1370
1261	1365	1367	1366	1370

Slope After - Hrs at 210°C (ev)

Sample No.	300°C for 78 hrs (ev)	145 hrs.	290 hrs.	458 hrs.
1258	0.3291	0.3266	0.3244	0.3259
1259	0.3227	0.3269	0.3260	0.3271
1260	0.3249	0.3269	0.3259	0.3235
1261	0.3290	0.3270	0.3247	0.3251

Although there is evidence of stabilization, there is also evidence of contacts separating. It appears desirable to anneal at lower temperatures with the leads soldered on. If this is true, it would restrict annealing to temperatures below the melting point of the tin solder, 232°C.

7. Sizing of Thermistors

We felt that final size adjustment might be accomplished by grinding, vapor-blasting, or chemical-etching techniques. The purpose of this adjustment is to obtain a given value of resistance at 25°C with an error of not over ±2%. The thermistor dice would be cut larger in size than actually necessary and material would be removed by one of the three techniques mentioned. The material removed would be continued until a resistance reading indicated that the thermistor was at the proper resistance level. This adjustment should not affect the temperature sensitivity or temperature-resistance ratios. So far, we have tried two of the techniques mentioned: vapor blasting and grinding.

The vapor-blasting unit tried was a S.S. White industrial air-abrasive unit. Cutting is effected by a high-speed stream of abrasive alumina particles, which are propelled by a gas such as CO_2 or nitrogen. This unit is effective for cutting the silicon; however, the propellant gas tends to cool the silicon during the cutting. This prevents any measurement of a resistance during the actural abrading operation, since the resistance is varying with the temperature of the thermistor. For these reasons, we have decided against vapor blasting as a technique for size adjustment of thermistors.

The other technique of size adjustment tried was that of grinding with a high-speed dentist-type drill and a diamond bit. The drill is driven by a flexible cable and has a top speed of about 12,000 rpm. A series of 4 x 4 x 1mm thermistors was adjusted toward 525 ohms at 0°C. The samples were embedded in paraffin wax and ground under ice water until the resistance as read on a vacuum tube volt meter reached approximately 525 ohms. Wheatstone bridge measurements on the thermistors were:

530 ohms	514 ohms	517 ohms
519 ohms	535 ohms	530 ohms
526 ohms	528 ohms	534 ohms

All, except possibly one, were within the ±2%. Another series was adjusted to 565 ohms at 0° and read 564, 567, and 571 ohms. Since the grinding is done under ice water, measurements of resistance can be made during the grinding operation. If a slight elevation in temperature occurs during the grinding, the thermistors reach 0°C immediately upon removal of the grinding tool. Smaller sizes, of course, would be more difficult to adjust.

Size adjustment by high-speed diamond grinding was selected as the pilot line production technique. Pilot line experience proved that thermistors on the order of 2 x 2 x 1mm could be easily adjusted to within 1% of a standard thermistor. In the pilot line set-up the thermistor being adjusted is compared to a standard by the ratio technique described earlier. The standard thermistor is mounted in the same silicone oil bath as the thermistor being adjusted. The P-type contract samples were adjusted

at room temperature. The N-type contract samples were adjusted at about 100°C. Adjusting by the ratio technique seems to proceed better at resistances below 10,000 ohms.

Chemical etching has not been tried as a possible technique for material removal because we have not been able to select a suitable etching solution or technique.

8. Manufacturing Process for Gold-Doped P-Type Silicon

A 28-step manufacturing process was developed for producing gold-doped P-type silicon thermistors. The unbalanced pilot line was operated according to this process while producing the 400 contract samples of P-type thermistors. The 28 steps are outlined below:

1. Determine necessary starting silicon resistivity.

2. Purchase monocrystalline rod from a commercial supplier, or prepare the same.

3. Check resistivity profile with 4-point probe.

4. Prepare rod for zone leveling: Etch 1:3 HF/HNO_3, water, dry.

5. Zone level with high-purity gold.

6. Cut three wafers from seed end, chuck end, and center.

7. Prepare three wafer-size thermistors from these slices and measure resistance at 25°C.

8. Calculate desired thickness of production wafers based on resistivity of the three trial wafers and dicing tool sizes.

9. Cut remaining zone-leveled rod into wafers.

10. Wash with alcohol, acetone, alcohol.

11. Lap wafers with 180-C silicon carbide paper.

12. Wash with water, wipe with paper to remove fine particles.

13. Wash successively with acetone, alcohol, water, HF, water, alcohol.

14. Vacuum deposit aluminum on wafers.

15. Alloy aluminum to silicon at 580-630°C.

16. Etch wafers with concentrated HF-water.

17. Wipe with paper, wash with water, HF, water.

18. Immerse wafers briefly in boiling ammonium hydroxide.

19. Nickel plate wafers by electrodeless technique at 96°C.

20. Heat treat at 210°C overnight in argon or nitrogen.

21. Recheck resistivity of several wafers with pressure contacts.

22. Determine final dice size.

23. Dice wafers.

24. Solder leads to dice with tin at 240°C-250°C.

25. Wash with methyl alcohol.

26. Adjust size of thermistors by high-speed diamond grinding comparing resistance to resistance of a standard thermistor.

27. Determine final temperature-resistance behavior at a minimum of three temperatures.

28. Paint and bake at 210°C.

Each step is discussed in more detail below:

Step 1 - Determine the necessary starting silicon resistivity.

The resistance of a thermistor will follow the equation,

$$R = \rho \frac{L}{A} \quad \text{Equation No. 1}$$

R = resistance of thermistor in ohms

ρ = resistivity of thermistor material in ohm cm

L = length of the thermistor between electrodes in cm

A = the cross sectional area of the thermistor in cm^2.

If we know the resistance and approximate size of a desired thermistor, it is possible to calculate the resistivity of the gold-doped silicon to be used in the device by this equation. Then using the relationship shown in Graph 14 it is possible to determine the necessary starting silicon resistivity. These curves were determined experimentally by doping various resistivities of P-type silicon with 0.15 grams of high-purity gold in the zone-leveling process. The rod diameters were 7/8 to 1", the estimated weight of the molten zone was 20 grams. 0.15 grams of gold was found to be the maximum amount that could be added to such a zone without causing polycrystallinity problems.

Step 2 - Purchase monocrystalline rod from a commercial supplier, or prepare the same.

The silicon being used in this process can be purchased from any one of a number of commercial suppliers. Presently, we are purchasing single-crystal silicon from Merck & Co. in Rahway, New Jersey. We have been

Graph 14

FINAL ZONE LEVELED RESISTIVITY - OHM CM

INITIAL RESISTIVITY - OHM CM P-TYPE
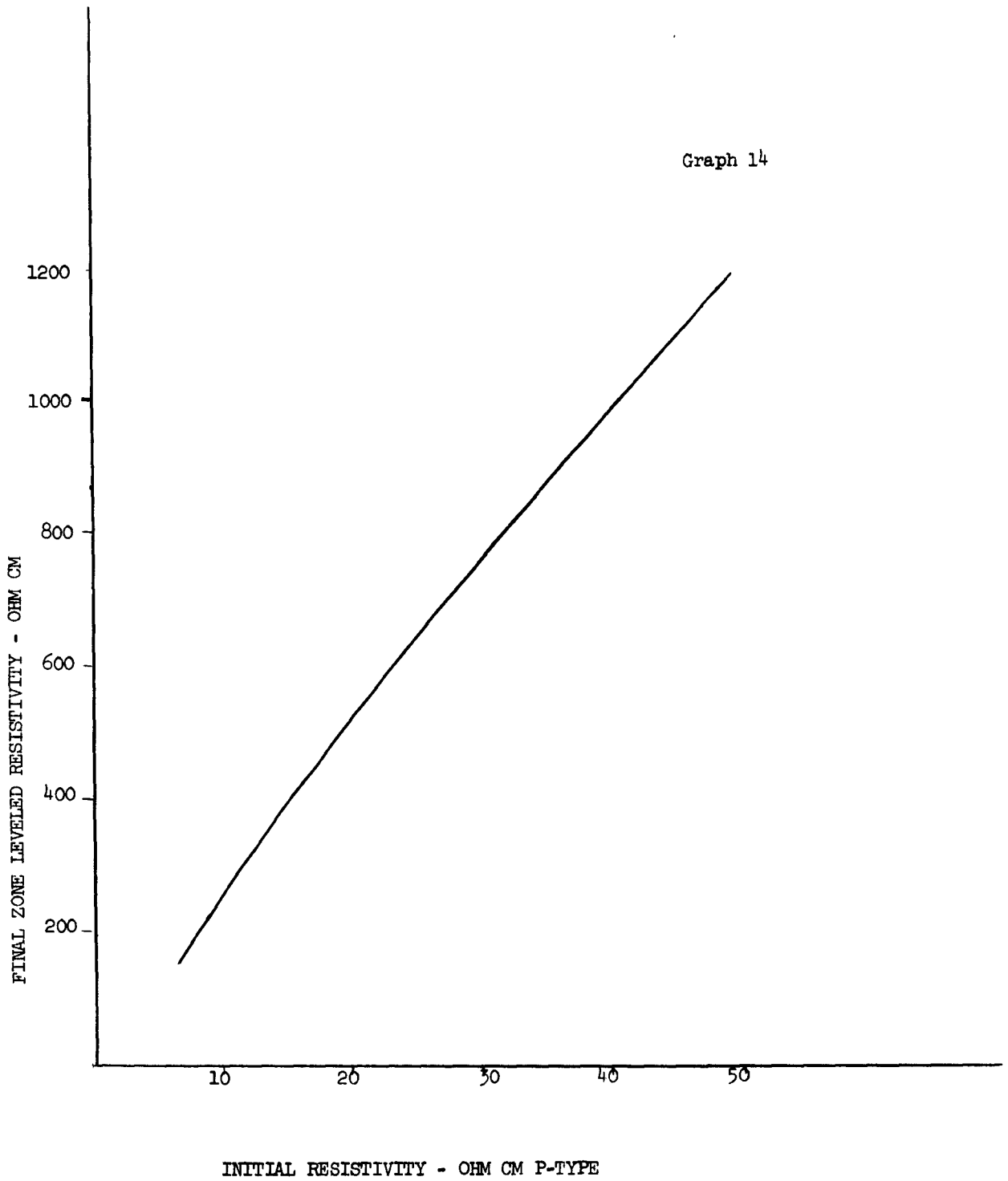
purchasing material within ±25% of a given resistivity value. Material of ±10% resistivity variance can be obtained at a higher price. However, we have found that there are enough process-control variables to allow the use of the ±25% material. Of particular importance is the size adjustment which allows the up-grading of the resistance of any thermistor to a higher value.

Step 3 - Check resistivity profile with 4-point probe.

This is a standard 4-point probe measurement, commonly used for measuring silicon under 1000 ohm cm. This step could be eliminated once there is good agreement between supplier and purchaser on resistivity levels.

Step 4 - Prepare rod for zone leveling: Etch 1 to 3 HF/HNO₃, dry.

The rod is etched in a mixture of one volume of concentrated (49%) HF to 3 volumes of concentrated (70%) nitric acid until the surface is clean and shining. It is then rinsed thoroughly in distilled, deionized water of one megohm cm or greater resistivity. Droplets of water are removed from the rod by blowing with high-purity argon. The rod is further dried under an infrared lamp on a thoroughly clean quartz pedestal.

Step 5 - Zone level with high-purity gold.

This is a standard zone-refining procedure in which high-purity gold is used as a dope between the seed and the rod. The gold is melted into the first zone as the seed and the rod are fused together by means of radio-frequency heating. Proper matching of the seed and rod must be made in the case P-type silicon. The resistivity of the seed should be approximately the same as that of the rod.

The zone-leveling pass is made at the rate of about 8 inches per hour. If the rod does not go single on the first pass, it should be re-doped before the second pass in order to obtain the same amount of residual gold.

Step 6 - Cut three wafers from seed end, chuck end, and center.

After zone leveling, the resistance of the gold-doped silicon is normally so high that the resistivity of the material cannot be checked easily by any simple 4-point or 2-point probe technique. We check the resistance of a rod at the various points mentioned by cutting wafers and fabricating large area devices from them. Because the area is large, the resistance of the device will tend to be low even for large resistivities. The thickness of the wafer is determined on the basis of the anticipated resistivity and the resistance of the devices to be made. The crystal is cemented to a ceramic block with jewelers' wax. After being cut, it is left oriented on the high-speed diamond saw. Further cuts can be made parallel to those already made.

Step 7 - Prepare three wafer-size thermistors from these slices and measure the resistance at 25°C.

The wafers are aluminum deposited, alloyed, etched, and nickel-plated. Pressure contacts are made. The resistance of these wafers is then measured with a Wheatstone bridge in a 25 ± 0.01°C bath. From the resistance and the physical dimensions of the wafers, the resistivity of the silicon is calculated according to Equation No. 1.

Step 8 - Calculate the desired thickness of production wafers based on resistivity of three trial wafers and dicing tool sizes.

This calculation is made again using Equation No. 1. Normally, there will be only certain dicing tool sizes available. Presently, for instance, we are using dicing tools 2-1/2, 3, and 3-1/2mm in diameter. More sizes could be carried for dicing purposes. Normally, the thickness of the production wafers is calculated to be about 10% less than that defined in Equation No. 1. This means that the resistance of the devices will be less than the desired value. However, later in the size-adjustment step, the resistance of the devices can be up-graded to higher values. It is desirable to have the peak of the product-resistance distribution below the desired-resistance value so that only a small portion or none of the devices fall above the desired value.

Step 9 - Cut remaining zone-leveled rod into wafers.

The zone-leveled rod which was left oriented on the diamond saw is then cut into wafers of the thickness calculated in Step 8.

Step 10 - Wash with alcohol, acetone, alcohol.

This step is to remove any traces of jewelers' wax, oil or other impurities which might be present as a result of diamond sawing.

Step 11 - Lap wafers with 180-C silicon carbide paper.

The wafers are lapped by hand under a metal weight making strokes in one direction only across the wafer.

Step 12 - Wash with water, wipe with paper to remove fine particles.

This treatment is used primarily to remove impurities, mainly particulate, which have collected on the silicon as a result of lapping. Wiping with paper seems to be necessary to remove all traces of fine matter. Some particles seem to remain even after the water washing.

Step 13 - Wash successively with acetone-methanol-water-conc. HF-water-methanol.

This step is used to prepare the wafer surfaces for aluminum deposition. It removes impurities such as grease, finger oil, oxide

film etc. which might interfere with a good aluminum deposition. Whereas good thermistors might be made by eliminating some of these steps, we feel that the most consistent results will be obtained by using all of them.

Beginning with this step and until the wafers are finally nickel plated, the circular surfaces should not be touched by the fingers or mechanical holders such as forceps. A mark, made by a forcep for instance, can result in poor adhesion of the aluminum or nickel coatings.

Step 14 - Vacuum deposit aluminum on wafers.

In this step a wafer or several wafers are mounted in a vacuum chamber above a densified graphite crucible containing high purity aluminum. The chamber is pumped down until the vacuum is below 8.5 x 10^{-5}mm Hg. The aluminum is flashed by means of a R-F heating coil around the graphite crucible. Other heating techniques could be used. The initial flash in our equipment lasts for 35 seconds. After a 5-minute cooling period another 35-second flash is made. After cooling the chamber is opened and the wafer or wafers are reversed so that the previously un-exposed sides are now exposed. The process is then repeated so that both sides of the wafers are deposited. Normally we deposit 0.3 to 0.5 milli-grams of aluminum per side of a wafer which is 7/8" to 1" in diameter. This amounts to 0.4 to 0.8 milligrams per square inch of surface.

Step 15 - Alloy aluminum to silicon at 580 to 630°C.

In this step the aluminum-deposited wafers are put into a homemade quartz-tube furnace under a helium ambient. Argon or nitrogen could probably be used also. The furnace is heated up and the alloying time is taken as the time the temperature remains above 580°C and below 630°C. Normally an alloying time of 20 minutes is used. Any furnace capable of these temperatures and an inert ambient could be used. The wafers are cooled under the helium ambient to prevent oxide formation.

Step 16 - Etch wafers with concentrated HF.

In this step, the aluminum-alloyed wafers, which have been allowed to cool, are etched in concentrated 49% HF. This etching not only removes oxide, which is formed on the aluminum-silicon surface, but also removes any excess aluminum which may be on the surface.

Step 17 - Wipe with paper, wash with water-conc. HF-water.

The wafer is wiped with paper to remove a blackish deposit formed in the previous HF treatment. The second HF treatment does not produce a blackish deposit. Water removes traces of HF and ionic impurities.

After the washings and HF treatments, the wafers are not exposed for any lengthy periods to the atmosphere. Exposure can result in an oxide film and subsequent poor adhesion of the metal platings. The wafers are kept under the solutions and transferred quickly from one to the other. Transfer to the ammonium hydroxide of Step 18 is also rapid.

Step 18 - Immerse wafers briefly in boiling ammonium hydroxide.

The wafers are immersed until the first signs of reaction are noted visually. This is usually a slight bubbling on the surface. They are then transferred rapidly to the nickel-plating solution with little atmospheric exposure.

Step 19 - Nickel plate wafers by electrodeless technique at 96°C.

The wafers are transferred very rapidly from the boiling ammonium hydroxide solution to the nickel-plating solution at about 96°C having the following formulation:

	gms/liter
Nickel Chloride- - - - - - - - -	30
Sodium Hypophosphite- - - - - -	10
Sodium Citrate- - - - - - - - -	65
Ammonium Chloride- - - - - - - -	50

Add ammonium hydroxide until the solution turns from green to blue (7 to 8 pH)

The pH is maintained at about 7 during the plating procedure which usually lasts for less than five minutes. During this time, approximately 0.0095 gram of nickel is plated on each wafer.

Step 20 - Heat treat at 210°C overnight in argon or nitrogen.

This step can be done in any conventional oven which can be fitted with an argon or nitrogen supply. It is done primarily to stabilize the resistance of the unit and to bring about slight changes which sometimes occur at the beginning of the annealing period.

Step 21 - Recheck resistivity of several wafers with pressure contacts.

The number of wafers rechecked in this step usually depends upon the amount of resistivity variance that is expected from the measurements made in Step 7. If the measurements there indicated a great variance in resistivity, perhaps every other wafer should be checked. If the measurements indicated a very uniform resistivity, this step could be eliminated. Contacts are made with pressure, usually under a spring-type clamp. No soldered connection is made. We have found that resistivities obtained by this technique check well with those obtained in Step 7.

Step 22 - Determine final dice size.

Again, we rely on Equation No. 1. At this point the resistivity and thickness of the device are fixed and only the area is to be determined. If the dice are to be circular the diameter is to be chosen to coincide with a dicing tool which is available, and as mentioned previously, to yield devices which are on the low side of the desired resistance value.

Step 23 - Dice wafers.

For circular dice we send the plated wafer to Semiconductor Specialties, Corp., Lodi, New Jersey, for ultrasonic dicing. The equipment used for dicing is a Cavitron ultrasonic dicer. This is standard equipment in the semiconductor industry. The dicing could be done here if we purchased the equipment. For a 2-1/2 mm diameter dice size we obtain approximately 50 to 55 dice per wafer. For 3-1/2 mm diameter size we obtain approximately 20-25 dice per wafer.

For square, rectangular or other straight-edge dice, we use the high-speed diamond saw and crosscut the wafers in the proper manner. We have had no indication that shape affects the temperature response of these devices.

Step 24 - Solder leads to dice with tin at 240°C-250°C.

The thermistor dice are mounted in a Teflon jug and tinned copper leads are brought up to the nickel-plated surfaces of the thermistors. Other lead material could be used. Flux is applied to the plated surfaces and jig and thermistor are dipped into a tin pot at 240°C-250°C. The thermistor is held in the tin just long enough for the tin to wet the thermistor and lead. Too long a period of time in the solder can result in a separated contact.

Other solders might be used. We use tin because of an upper operating temperature of 200°C.

Step 25 - Wash with alcohol.

After removal from the solder pot, the thermistors are washed with methyl alcohol to thoroughly remove any remaining traces of flux and to clean the surface.

Step 26 - Adjust size of thermistors by high-speed diamond grinding comparing resistance-to-resistance of a standard thermistor.

Thermistors which are below the desired resistance value and need adjustment are mounted near a standard thermistor of the proper resistance. Both thermistors are submerged below the surface of a silicone oil bath. Since the adjustment is made by comparing the resistance of a thermistor being adjusted to the resistance of a standard thermistor, temperature control of the oil bath is not necessary. On P-type thermistors we usually adjust at room temperature. The standard thermistor and the thermistor being adjusted are mounted in opposite ratio arms of a Wheatstone bridge. Silicon is abraded away from the side of the thermistor until the resistance reaches the desired value. Abrasion is accomplished by a diamond bit in a 12000 rpm dentist-type drill, although other abrading techniques could work. The operator abrades until the galvanometer reaches 0, indicating no difference between the standard thermistor and the reference thermistor.

Step 27 - Final determination of temperature-resistance behavior at a minimun of three temperatures.

It is felt that measurement at three temperatures can be used to define the temperature-resistance behavior of these thermistors on a production basis, once a base curve has been carefully determined.

For gold-doped P-type silicon these temperatures might be 25°C, 0°C, and -60°C. Thermistors which are on the low-resistance side according to this test can be sent for readjustment.

These measurements can be made by comparing the resistance of the production thermistor to the resistance of a well determined standard thermistor.

Step 28 - Paint and bake at 210°C.

The final painting is normally done by hand in order to get as much paint as possible on the edges of the thermistor. Spraying or dipping usually results in a deficiency of paint near the edges of the thermistor. Presently, we are using a white silicone enamel for painting. However, we believe that a room-temperature vulcanizing silicone rubber, such as Dow Corning RTV 731, if applied in a thin film, will withstand extremes of temperatures more readily. Thinness of film is needed in order to obtain a desirable time constant of response.

Normally we apply two coats of silicone enamel and bake 1 hour for the 1st coat and 2 hours for the second coat. Baking time or temperature in not critical as long as the coating cures sufficiently.

Experience with the described production process could lead to the elimination of certain steps such as 6, 7, 8, and 21. These are check points which might be dropped as knowledge is gained on the product output for a given silicon input. Although some short cuts might be made in the process, we feel the most consistent results will be obtained by following the described producedure.

In the following section is a series of photographs demonstrating the most important steps in the process. These show equipment and techniques used in the specified steps

Step 3

Equipment for measuring resistivity of silicon rods showing rod on 4-point probe table, power supply, galvanometer and potentiometer.
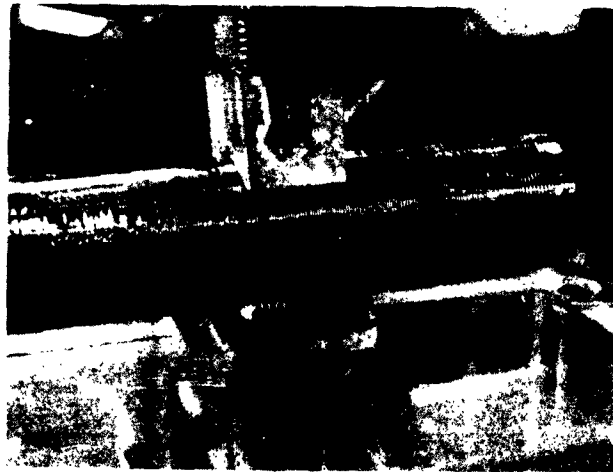
Closeup of silicon rod on 4- point probe.

Step 5

Zone leveling of gold in silicon rod. An argon ambient
is being used in a Lindberg float zone refiner.

Step 7 (21)
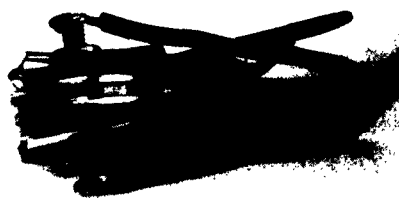
Mounting of wafer size thermistors in pressure clamps for resistivity measurement.

Step 11
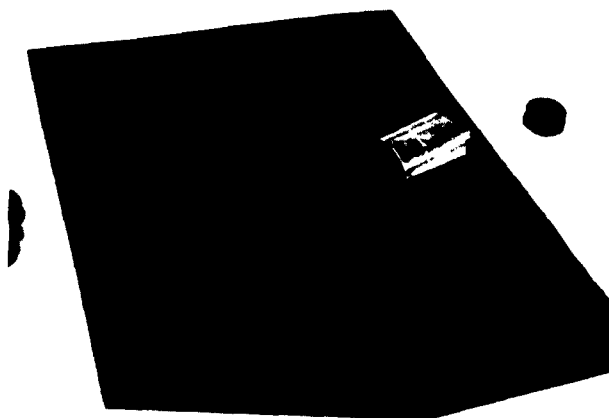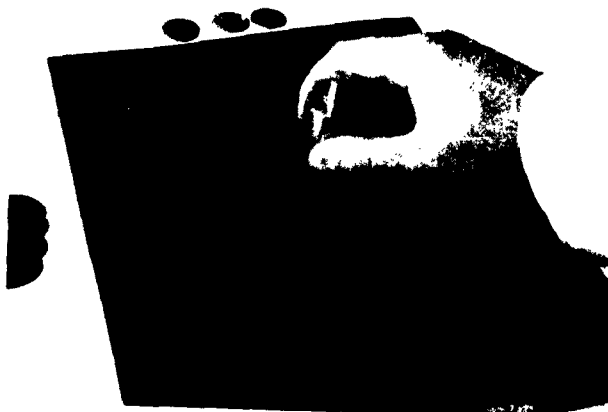
Lapping of wafers in one direction on 180 C silicon carbide paper. Wafer is mounted under metal weight.

Step 14
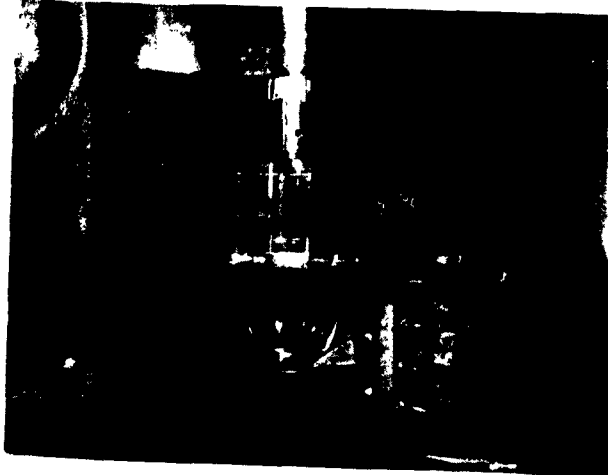
Apparatus for vacuum deposition of aluminum on a single silicon wafer. Apparatus is mounted in chamber of a Kinney high vacuum float zone refiner. It is setting on a single turn secondary of a transformer type RF coil.

Umbrella shaped holder for seven wafers during vacuum deposition. This is also mounted in Kinney high vacuum chamber.

Step 15
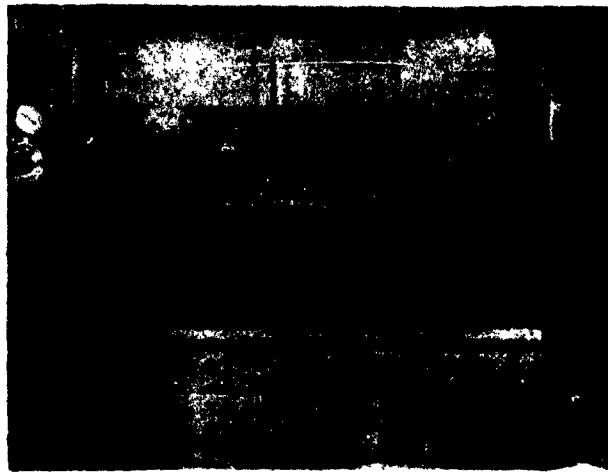
Homemade furnace for alloying aluminum to silicon at 580-630°C.
Included is helium gas supply, Variac for power control and potentio-
meter for measuring.
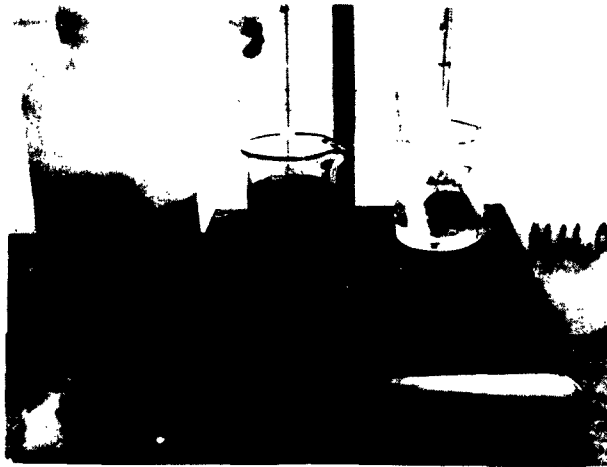
Immersion of aluminum alloyed wafers in boiling ammonium hydroxide.

Nickel plating of wafers at 96°C.

Cutting of square dice on high speed diamond saw by crosscutting technique. Silicon wafer is embedded in jeweler's wax to prevent clipping of edges.

Step 23

Square dice (2 x 2 mm) as cut on high speed diamond saw by crosscutting technique. Wafer is completely imbedded in jewelers wax.
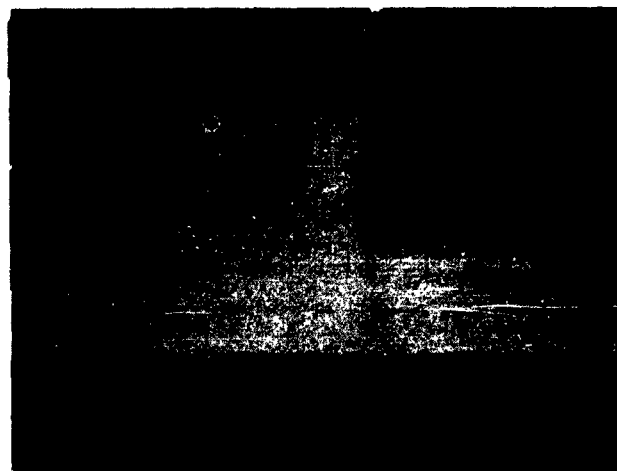
Cylindrical dice as cut on an ultrasonic dicer. These measure 2.5 mm in diameter by 5 mm in length. Other sizes are easily obtainable.

Closeup of Teflon jig with thermistor element wedged into central slot. Timed copper leads are butted against the nickel plated electrodes.
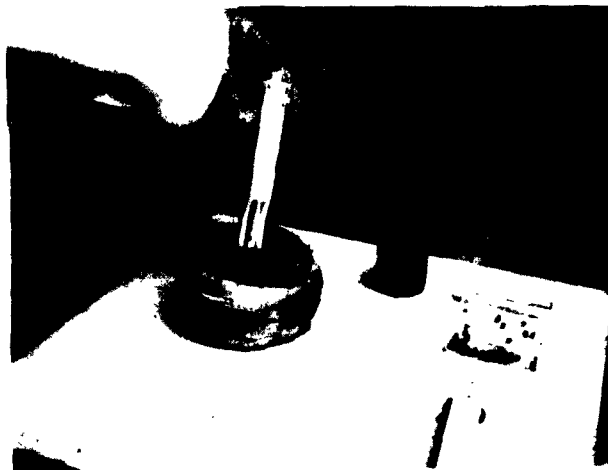
Dipping of Teflon jig with thermistor in molten tin to solder leads.

Step 26

Adjusting N-type thermistor. Thermistor is ground and then lowered into silicone oil bath at 100°C and compared to standard thermistor.
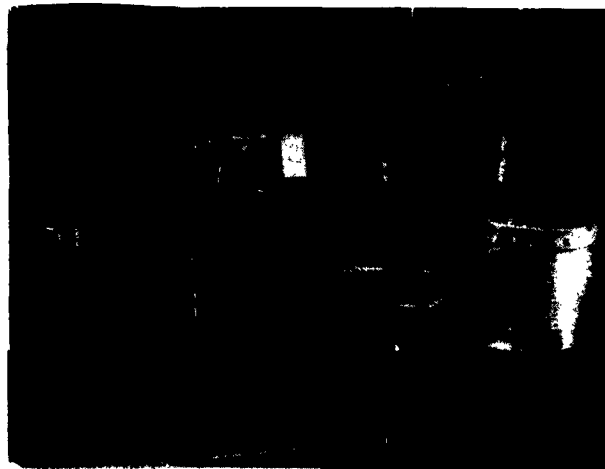
Complete size adjusting equipment showing electronic galvanometer, Wheatstone bridge, micro-amp meter, and oil bath.

Step 26

     Adjusting of P-type thermistors in silicone oil bath at room temperature. Thermistor being adjusted and standard thermistor are in opposite arms of Wheatstone bridge.

Step 27

Attaching Wheatstone bridge leads to thermistors in 25°C constant temperature bath.

Step 28

Hand painting of thermistors with white silicone enamel. Only
hand painting resulted is good coverage of the thermistor edges.

Example of Application of P-type Manufacturing Process

A monocrystalline silicon rod was purchased from Merck & Co. The resistivity and diameter profiles are given below. The first measurements were made 6 mm from the seed end of the crystal. The remaining readings were made at equal intervals along the 3-11/16" crystal.

TABLE 21

Diameter in mm	P-type Resistivity in ohm cm
22.4	15.6
22.6	15.9
22.7	15.1
22.5	14.1
22.8	25.7

The rod and seed were cleaned and etched with a solution of 1 volume concentrated HF (49%) and 3 volumes concentrated HNO_3 (70%). They were blown dry with argon. The seed and rod were set up in an argon ambient zone refiner for float-zone leveling of gold. The seed used in this case was 22.2 ohm cm P-type. 0.1515g of high-purity gold was inserted as the dope between the seed and the rod. The seed, rod and dope were fused together in the first molten zone and the zone was passed through the rod at the rate of 8 inches per hour. At the end of the pass the rod was 100% monocrystalline.

Three wafers, 2.2 mm thick were cut from the seed end, center and chuck end of the zone-leveled rod. The wafers were deposited with aluminum and alloyed at 580°-630°C. Nickel plating was applied over the aluminum. The aluminum and nickel plating on the edges of the wafers were sanded away to prevent short circuiting. Pressure contacts were made. The wafers were immersed in a 25°C bath and measured. They read 19.5, 19.3 and 16.7 ohms respectively.

It was desired to make units of 500 ohms at 25°C from this material. Using the equation $R = \frac{\rho L}{A}$ it was determined to cut the remaining rod into wafers 2.2 mm thick. It was assumed that the final dice would be cut square with a diamond saw and measure 3 to 4 mm on a side.

The rod, which had been previously mounted on a ceramic block with jewelers wax and left oriented on the diamond saw, was cut into wafers 2.2 mm thick. Methyl alcohol was used to separate the jewelers' wax from the wafers. The wafers were then washed with acetone and alcohol. The wafers were hand lapped in one direction with 180-C silicon carbide paper. They were washed with water and wiped with paper to remove fine particles. Successive washings with acetone, methanol, water, conc. HF, water and methanol then followed. The wafers were prepared for aluminum deposition.

Aluminum was deposited on both sides of the wafers as described under Step 14. Handling very carefully so as not to mar the surface the wafers were transferred to the alloying furnace. Here they were alloyed under helium at a temperature of 580-630°C for 20 minutes. The wafers were allowed to cool in the helium ambient.

After cooling the wafers were etched in concentrated (49%) HF to remove oxide and excess aluminum from the surface. They were then wiped with paper and washed successively with water, conc. HF, and water. Immersion in boiling ammonium hydroxide, NH_4OH, then followed. When the first signs of visible reaction occurred on the surface, the wafers were transferred rapidly to the nickel-plating solution. Nickel plating was carried out as described in Step 19.

The plated wafers were heated at 210°C overnight in a nitrogen atmosphere. Of the 20 wafers which had been cut from the bar, 7 from spaced intervals were measured at 25°C with pressure contacts. These measured 19.5, 20.0, 19.9, 21.7, 19.3, 18.3, 16.5, 18.6 ohms respectively. These readings checked with the readings on the first three trial wafers. Wafer 15 which measured 16.5 ohms was considered for dicing to 500 ohms at 25°C thermistors. Using the physical dimensions and the equation $R = \rho \dfrac{L}{A}$ the resistivity, ρ, of the silicon in this wafer was calculated to be 282 ohm cm. Again using the equation and fixing R at 500 ohms, ρ at 282 ohm cm and l at 2.2 mm, the area, A, of a 500 ohm device would be 0.1240 cm² or a square of 3.5 mm on a side. Since it was desired to have the final devices fall below 500 ohms, square dice of 3.6 mm on a side were cut on the diamond saw. Leads were soldered to the dice with tin as described in Step 24. A washing with methyl alcohol followed.

The size of the thermistors was adjusted as described in Step 26 upgrading the resistance to 500 ohms at 25°C. Before adjusting, the thermistors from wafer 15 measured about 470 ohms. The resistance of the thermistors from this wafer were measured at 0, 25 and -58.5°C to determine the deviation from a standard curve. The results of these measurements are given below.

TABLE 22

Resistance in ohms at

Sample No.	25°C	0°C	-58.5°C
W-15-·1	500	1592	80,330
W-15- 2	499	1585	80,250
W-15- 3	499	1588	80,370
W-15- 4	500	1595	80,750
W-15- 5	502	1600	80,930
W-15- 6	500	1599	80,460
W-15- 7	500	1597	80,648
W-15- 8	500	1599	80,700
W-15- 9	501	1598	80,270
W-15- 10	500	1593	80,770
W-15- 11	500	1596	80,800
W-16- 12	501	1601	80,650
W-15- 13	500	1596	80,300
W-15- 14	501	1591	79,100
W-15- 15	500	1592	80,250

Only sample W-15-14 was of questionable resistance at -58.5°C. The thermistors were then coated with a film of white silicone enamel, baked 1 hour at 210°C, recoated and baked 4 hours at 210°C. The thermistors are then finished and ready for use.

The standard curve for these thermistors is given below:

TABLE 23

Temperature vs. Resistance -85°C. to +50°C.

Temp.°C.	Res. Ω	Temp.°C.	Res. Ω	Temp.°C.	Res. Ω
-85	1097K	-45	27.02K	- 5	2082
-84	980.9K	-44	25.05K	- 4	1974
-83	878.0K	-43	23.24K	- 3	1872
-82	786.9K	-42	21.58K	- 2	1776
-81	706.0K	-41	20.05K	- 1	1685
-80	634.1K	-40	18.64K	0	1600
-79	570.2K	-39	17.33K	1	1520
-78	513.3K	-38	16.14K	2	1445
-77	462.6K	-37	15.03K	3	1374
-76	417.3K	-36	14.01K	4	1307
-75	376.9K	-35	13.06K	5	1243
-74	340.7K	-34	12.19K	6	1184
-73	308.4K	-33	11.38K	7	1127
-72	279.3K	-32	10.63K	8	1074
-71	253.3K	-31	9941	9	1024
-70	229.9K	-30	9298	10	976.0
-69	208.9K	-29	8703	11	931.0
-68	190.0K	-28	8150	12	888.4
-67	172.9K	-27	7636	13	848.0
-66	157.5K	-26	7159	14	809.9
-65	143.7K	-25	6716	15	773.7
-64	131.1K	-24	6303	16	739.4
-63	119.8K	-23	5919	17	706.9
-62	109.5K	-22	5561	18	676.1
-61	100.2K	-21	5228	19	646.9
-60	91.80K	-20	4917	20	619.1
-59	84.15K	-19	4627	21	592.8
-58	77.20K	-18	4357	22	567.8
-57	70.88K	-17	4104	23	544.0
-56	65.14K	-16	3868	24	521.5
-55	59.90K	-15	3648	25	500.0
-54	55.13K	-14	3441	26	479.6
-53	50.78K	-13	3248	27	460.2
-52	46.81K	-12	3068	28	441.7
-51	43.18K	-11	2898	29	424.1
-50	39.86K	-10	2740	30	407.3
-49	36.83K	- 9	2591		
-48	34.05K	- 8	2452		
-47	31.50K	- 7	2321		
-46	29.17K	- 6	2198		

9. Manufacturing Process for Gold-Doped N-type Silicon

A twenty-four step manufacturing process was developed for producing gold-doped N-type thermistors. The unbalanced pilot line was operated according to this process while producing the 200 contract samples of N-type thermistors.

The twenty-four steps are outlined below:

1. Determine necessary starting silicon resistivity.

2. Purchase monocrystalline rod from a commercial supplier, or prepare the same.

3. Check resistivity profile with 4-point probe.

4. Prepare rod for zone leveling: Etch 1:3 HF/HNO_3, dry.

5. Zone level with high-purity gold.

6. Cut three wafers from seed end, chuck end, and center.

7. Prepare three wafer-size thermistors from these slices and measure resistance at 25°C.

8. Calculate desired thickness of production wafers based on resistivity of the three trial wafers and dicing tool sizes.

9. Cut remaining zone-leveled rod into wafers.

10. Wash with alcohol, acetone, alcohol.

11. Lap wafers with 180-C silicon carbide paper.

12. Wash with water, wipe with paper to remove fine particles.

13. Wash successively with acetone, alcohol, water, conc. HF, water.

14. Immerse wafers briefly in boiling ammonium hydroxide.

15. Nickel plate wafers by electrodeless technique at 96°C.

16. Heat treat at 210°C overnight in argon or nitrogen.

17. Recheck resistivity of several wafers with pressure contacts.

18. Determine final dice size.

19. Dice wafers.

20. Solder leads to dice with tin at 240°C.

21. Wash with methyl alcohol.

22. Adjust size of thermistors by high-speed diamond grinding comparing resistance to resistance of a standard thermistor.

23. Determine final temperature-resistance behavior at a minimum of three temperatures.

24. Paint and bake at 210°C.

Many of these steps are the same as in the case of gold-doped P-type silicon. Only the steps which are different will be discussed in more detail below:

Step 1 - Determine the necessary starting silicon resistivity.

The resistance of a thermistor will follow the equation,

$$R = \rho \frac{L}{A} \quad \text{Equation No. 2}$$

R = resistance of thermistor in ohms

ρ = resistivity of thermistor material in ohm cm.

L = length of the thermistor between electrodes in cm.

A = the cross sectional area of the thermistor in cm².

If we know the resistance and approximate size of a desired thermistor, it is possible to calculate the resistivity of the gold-doped silicon to be used in the device by this equation. Then using the relationship shown in Graph 15, it is possible to determine the necessary starting silicon resistivity. These curves were determined experimentally by doping various resistivities of N-type silicon with 0.15 grams of high-purity gold in the zone-leveling process. The rod diameters were 7/8 to 1", the estimated weight of the molten zone was 20 grams. 0.15 grams of gold was found to be the maximum amount that could be added to such a zone without causing polycrystallinity problems.

Step 2 - Purchase monocrystalline rod from a commercial supplier, or prepare the same.

Step 3 - Check resistivity profile with 4-point probe.

Step 4 - Prepare rod for zone leveling: Etch 1 to 3 HF/HNO₃, dry.

Step 5 - Zone level with high-purity gold.

This is a standard zone-refining procedure in which high-purity gold is used as a dope between the seed and the rod. The gold is melted into the first zone as the seed and the rod are fused together by means of radio-frequency heating.

Graph 15

FINAL ZONE LEVELED RESISTIVITY - OHM CM.

INITIAL RESISTIVITY - OHM CM. N-TYPE
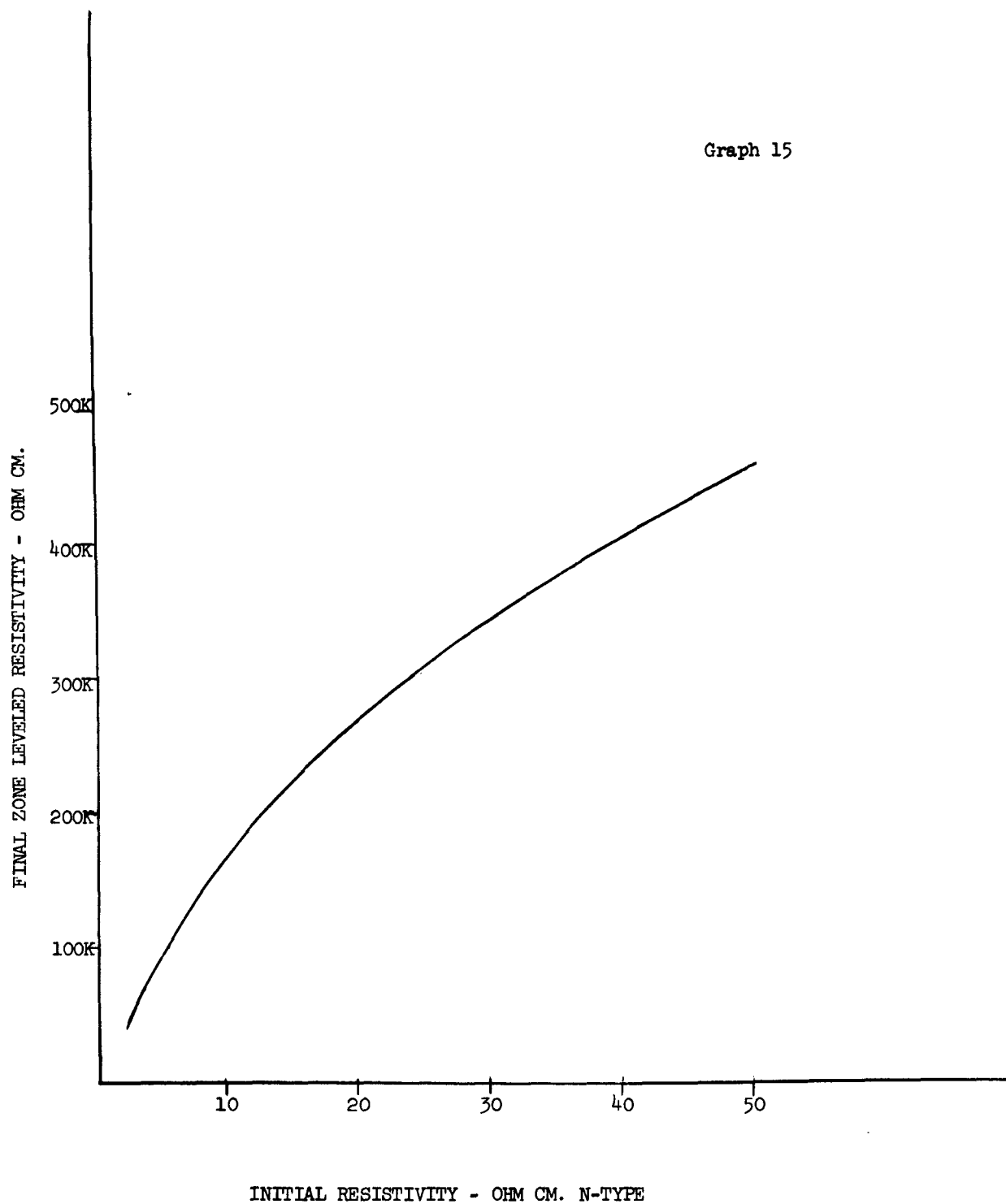
The resistivity of the seed should be smaller than the resistivity of the rod by an amount depending upon the amount of the seed that is fused into the first zone. This level has to be determined by experience with the float-zone leveling process. Normally, the amount of N-type impurity in the first zone should be equal to approximately 3 times that of N-type impurity that the zone will see as it passes up the rod.

The zone-leveling pass is made at the rate of about 8 inches per hour. If the rod does not go single on the first pass, it should be re-doped before the second pass in order to obtain the same amount of residual gold.

Step 6 - Cut three wafers from seed end, chuck end, and center.

Step 7 - Prepare three wafer-size thermistors from these slices and measure the resistance at 25°C.

Step 8 - Calculate the desired thickness of production wafers based on resistivity of three trial wafers and dicing tool sizes.

Step 9 - Cut remaining zone-leveled rod into wafers.

Step 10- Wash with alcohol, then acetone, alcohol.

Step 11- Lap wafers with 180-C silicon carbide paper.

Step 12- Wash with water, wipe with paper to remove fine particles.

Step 13- Wash successively with acetone-methanol-water-conc. HF-water.

This step is used to prepare the wafer surfaces for nickel plating. It removes impurities such as grease, finger oil, oxide film, etc., which might interfere with a good aluminum deposition. Whereas, good thermistors might be made by eliminating some of these steps, we feel that the most consistent results will be obtained by using all of them.

Beginning with this step and until the wafers are finally nickel plated, the circular surfaces should not be touched by the fingers or mechanical holders such as forceps. A mark, made by a forcep, for instance, can result in poor adhesion of the plating.

Step 14 - Immerse wafers briefly in boiling ammonium hydroxide.

The wafers are immersed until the first signs of reaction are noted visually. This is usually a slight bubbling on the surface. They are then transferred rapidly to the nickel-plating solution with little atmospheric exposure.

After the washings and HF treatments the wafers are not exposed for any lengthy periods to the atmosphere. Exposure can result in an oxide film and subsequent poor adhesion of the metal plating. The wafers are kept under the solutions and transferred quickly from one to the other. Transfer to the ammonium hydroxide of Step 18 is also rapid.

Step 15 - Nickel plate wafers by electrodeless technique at 96°C.

Step 16 - Heat treat 210°C overnight in argon or nitrogen.

Step 17 - Recheck resistivity of several wafers with pressure contacts.

Step 18 - Determine final dice size.

Step 19 - Dice wafers.

Step 20 - Solder leads to dice with tin at 240°C.

Step 21 - Wash with alcohol.

Step 22 - Adjust size of thermistors by high-speed diamond grinding comparing resistance-to-resistance of a standard thermistor.

Step 23 - Final determination of temperature-resistance behavior at a minimum of three temperatures.

It is felt that measurement at three temperatures can be used to define the temperature-resistance behavior of these thermistors on a production basis, once a base curve has been carefully determined.

For gold-doped N-type silicon these temperatures might be 25°C, 100°C and 200°C. Thermistors which are on the low-resistance side according to this test can be sent for readjustment.

These measurements can be made by comparing the resistance of the production thermistor to the resistance of a well determined standard thermistor.

Step 24 - Paint and bake at 210°C.

Experience with the described production process could lead to the elimination of certain steps such as 6, 7, 8, and 17. These are check points which might be dropped as knowledge is gained on the product output for a given silicon input. Although some short cuts might be made in the process, we feel the most consistent results will be obtained by following the described procedure.

Example of Application of N-type Manufacturing Process

An N-type monocrystalline rod, 5-1/2" long and 7/8" in diameter was prepared for float-zone leveling. The resistivity profile was measured. The first reading was made 6mm from the seed end. The remaining readings were made at equally spaced intervals along the rod.

TABLE 24

N-Type Resistivity
in ohm cm

8.3
7.5
8.4
7.9
7.6
7.8
7.8
8.2

The rod and a seed, 640 ohm cm N-type, were etched in a solution of 1 volume of 49% HF to 3 volumes 70% HNO_3 to a bright-finish brown with argon and dried under infrared heat. The seed and rod were set up in an argon ambient zone refiner for float-zone leveling of gold. 0.1579 gms of high-purity gold was inserted as a dope between the seed and the rod. Also inserted was 0.0247 gms of a silicon phosphorous dope containing 14,000 ppb. phosphorous. The seed, rod and dope were fused together in the first molten zone and the zone was passed through the rod at the rate of 8 inches per hour. At the end of the pass the rod was 100% monocrystalline.

Three wafers, 1.2mm thick were cut from the seed end, center and chuck end of the zone-leveled rod. They were cleansed, lapped and plated with nickel by the electrodeless technique. The nickel plating on the edges of the wafers was sanded away to prevent short circuiting. Pressure contacts were made. The wafers were immersed in a 25°C bath and measured. They read 4864, 4848 and 4882 ohms respectively.

It was desired to make units of 500,000 ohms at 25°C from this material. Using the equation $R = \rho \dfrac{L}{A}$ it was determined to cut the remaining rod into wafers 1.2mm thick. It was assumed that the final dice would be cut square with a diamond saw and measured about 2mm on a side.

The rod, which had been previously mounted on a ceramic block with jewelers' wax and left oriented on the diamond saw was cut into wafers 1.2mm thick. Methyl alcohol was used to separate the jewelers' wax from the wafers. The wafers were then washed with acetone and alcohol. The wafers were hand lapped in one direction with 180-C silicon carbide paper. They were washed with water and wiped with paper to remove fine particles. Successive washings with acetone, methanol, water, conc. HF, and water then followed. The wafers were prepared for nickel plating.

Immersion in boiling ammonium hydroxide, NH_4OH, then followed. When the first signs of visible reaction occurred on the surface,

the wafers were transferred rapidly to the nickel-plating solution. Nickel plating was carried out as described in Step No. 15.

The plate wafers were heated at 210°C overnight in a nitrogen atmosphere. Of the wafers which had been cut from the bar, 6 from spaced intervals were measured at 25°C with pressure contacts. These measured 4855, 4889, 4916, 4920, 4994, 4873 ohms respectively. These readings checked with the readings on the first three trial wafers. Wafers 1 and 2 which measured 4864 and 4848 ohms were considered for dicing to 400,000 ohms at 25°C thermistors. Using the physical dimensions and the equation $R = \rho \dfrac{L}{A}$ the resistivity, ρ, of the silicon in this wafer was calculated to be 150,000 ohm cm. Again using the equation and fixing R at 500,000 ohms, ρ at 150,000 ohm cm and L at 1.2mm, the area, A, of a 500,000 ohm device would be 0.040 cm^2 or a square of 2.0mm on a side. Since it was desired to have the final devices fall below 500,000 ohms, square dice of 2.1mm on a side were cut on the diamond saw. Leads were soldered to the dice with tin as described in Step 20. A washing with methyl alcohol followed.

The size of the thermistors was adjusted as described in Step 22 up-grading the resistance to 500,000 ohms at 25°C. Before adjusting, the thermistors measured about 430,000 ohms.

The resistance of the thermistors from this wafer was measured at 25, 60, 100 and 200°C to determine the fit to a standard curve. The results of these measurements are given below.

<div align="center">

TABLE 25

Resistance in ohms at
</div>

Thermistor No.	25°C	59.7°C	100.1°C	200.0°C
W-C-1	499K	58.9K	8140	279
W-C-2	498K	58.5K	8160	273
W-C-3	496K	59.0K	8160	274
W-C-4	495K	58.1K	8140	274
W-C-5	495K	58.8K	8140	278
W-C-6	499K	58.9K	8130	277
W-C-7	491K	58.8K	8150	283
W-C-8	501K	59.2	8170	284
W-C-9	496K	58.7K	8090	274
W-C-10	494K	59.1K	8140	275

The thermistors were then coated with a film of white silicone enamel, baked 1 hour at 210°C, recoated and baked 4 hours at 210°C. The thermistors were finished and ready for use.

The temperature at which these thermistors show the most variation is at 200°C. Most of the variation in N-type thermistors occurs near 200°C. A master curve for these thermistors is given below.

TABLE 26

Temperature vs. Resistance 0°C. to 200°C.

Temp.°C.	Res. Ω	Temp.°C.	Res. Ω	Temp.°C.	Res. Ω	Temp.°C.	Res. Ω
0	3320K	51	96.02K	102	7498	153	1104
1	3057K	52	90.61K	103	7183	154	1069
2	2816K	53	85.53K	104	6884	155	1035
3	2596K	54	80.77K	105	6599	156	1002
4	2395K	55	76.30K	106	6327	157	969.8
5	2211K	56	72.11K	107	6067	158	939.1
6	2042K	57	68.17K	108	5820	159	909.6
7	1887K	58	64.46K	109	5584	160	881.1
8	1744K	59	60.98K	110	5359	161	853.7
9	1614K	60	57.71K	111	5144	162	827.2
10	1494K	61	54.63K	112	4938	163	801.7
11	1384K	62	51.74K	113	4742	164	777.0
12	1282K	63	49.01K	114	4555	165	753.3
13	1189K	64	46.44K	115	4376	166	730.4
14	1103K	65	44.02K	116	4205	167	708.3
15	1024K	66	41.75K	117	4042	168	686.9
16	950.8K	67	39.60K	118	3885	169	666.3
17	883.4K	68	37.57K	119	3736	170	646.4
18	821.3K	69	35.66K	120	3593	171	627.2
19	764.0K	70	33.86K	121	3456	172	608.7
20	711.0K	71	32.16K	122	3325	173	590.8
21	662.0K	72	30.55K	123	3200	174	573.5
22	616.7K	73	29.04K	124	3080	175	556.7
23	574.7K	74	27.60K	125	2965	176	540.6
24	535.9K	75	26.25K	126	2855	177	525.0
25	500.0K	76	24.97K	127	2750	178	509.9
26	466.7K	77	23.76K	128	2649	179	495.3
27	435.8K	78	22.61K	129	2552	180	481.2
28	407.1K	79	21.53K	130	2460	181	467.5
29	380.5K	80	20.50K	131	2371	182	454.3
30	355.9K	81	19.53K	132	2286	183	441.6
31	332.9K	82	18.61K	133	2204	184	429.2
32	311.6K	83	17.74K	134	2125	185	417.2
33	291.8K	84	16.91K	135	2050	186	405.7
34	273.3K	85	16.13K	136	1978	187	394.5
35	256.2K	86	15.38K	137	1909	188	383.7
36	240.2K	87	14.68K	138	1842	189	373.2
37	225.3K	88	14.01K	139	1778	190	363.0
38	211.4K	89	13.38K	140	1717	191	353.2
39	198.5K	90	12.77K	141	1658	192	343.6
40	186.4K	91	12.20K	142	1601	193	334.4
41	175.2K	92	11.66K	143	1547	194	325.5
42	164.7K	93	11.14K	144	1494	195	316.8
43	154.8K	94	10.65K	145	1444	196	308.4
44	145.7K	95	10.19K	146	1395	197	300.3
45	137.1K	96	9742	147	1349	198	292.4
46	129.1K	97	9321	148	1304	199	284.8
47	121.6K	98	8919	149	1261	200	277.3
48	114.5K	99	8537	150	1220		
49	108.0K	100	8174	151	1180		
50	101.8K	101	7827	152	1141		

10. Contract Sample Thermistors

Figure 20 is a photograph of typical thermistors prepared under the contract. Gold-doped P-type samples were prepared with resistances at 25°C of 4000, 5000 ohms and 500 ohms. The four and five thousand ohm samples were cylindrical in shape, being approximately 2.5mm in diameter by 2mm in length. The 500 ohm P-type samples measured approximately 3.8 x 3.8 x 2.3mm, the electrode area being square. These were the largest thermistors produced and had the most undesirable time constants of response. However, they were the easiest to adjust to a given resistance.

The gold-doped N-type samples made under the contract were 500K ohms at 25°C and measured 2x2x1mm. Again the electrodes were square and the dice were made by cross-cutting techniques on the high-speed diamond saw.

We are including in Tables 27 and 28 temperature-resistance curves for the 4000 and 5000 ohm P-type samples. The 500 ohm P-type and 500K N-type curves were given under the sections on process examples.
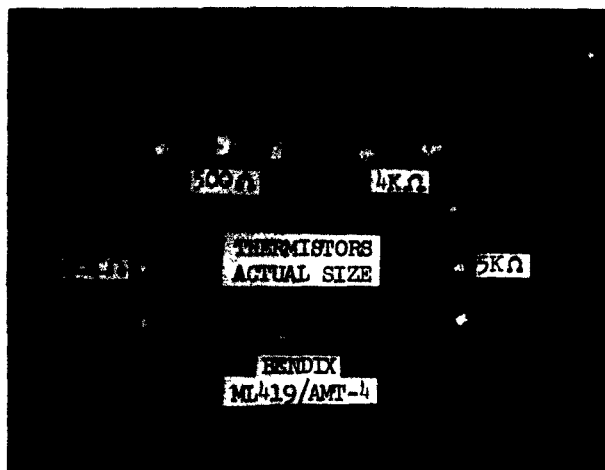
Finished thermistors, actual size.   Comparison is made
with a Bendix ML419/AMT-4 thermistor.

TABLE 27

Temperature vs. Resistance -85°C. to +30°C.

Temp.°C.	Res. Ω	Temp.°C.	Res. Ω	Temp.°C.	Res. Ω
-85	8525K	-45	212.9K	- 5	16.57K
-84	7625K	-44	197.4K	- 4	15.71K
-83	6828K	-43	183.2K	- 3	14.90K
-82	6122K	-42	170.1K	- 2	14.14K
-81	5495K	-41	158.1K	- 1	13.42K
-80	4938K	-40	147.0K	0	12.75K
-79	4442K	-39	136.8K	1	12.11K
-78	4000K	-38	127.4K	2	11.51K
-77	3606K	-37	118.7K	3	10.95K
-76	3255K	-36	110.6K	4	10.41K
-75	2940K	-35	103.2K	5	9911
-74	2659K	-34	96.33K	6	9437
-73	2407K	-33	89.96K	7	8989
-72	2182K	-32	84.07K	8	8566
-71	1979K	-31	78.61K	9	8166
-70	1797K	-30	73.55K	10	7787
-69	1633K	-29	68.86K	11	7429
-68	1486K	-28	64.50K	12	7091
-67	1353K	-27	60.45K	13	6770
-66	1233K	-26	56.69K	14	6466
-65	1125K	-25	53.19K	15	6179
-64	1027K	-24	49.93K	16	5906
-63	938.5K	-23	46.90K	17	5648
-62	858.4K	-22	44.08K	18	5402
-61	785.8K	-21	41.45K	19	5170
-60	719.9K	-20	38.99K	20	4949
-59	660.2K	-19	36.70K	21	4739
-58	605.8K	-18	34.56K	22	4540
-57	556.5K	-17	32.57K	23	4351
-56	511.5K	-16	30.70K	24	4171
-55	470.5K	-15	28.96K	25	4000
-54	433.2K	-14	27.33K	26	3837
-53	399.1K	-13	25.80K	27	3683
-52	368.0K	-12	24.37K	28	3535
-51	339.6K	-11	23.03K	29	3395
-50	313.6K	-10	21.77K	30	3261
-49	289.8K	- 9	20.60K		
-48	268.0K	- 8	19.49K		
-47	248.0K	- 7	18.45K		
-46	229.7K	- 6	17.48K		

TABLE 28

Temperature vs. Resistance -85°C. to +30°C.

Temp.°C.	Res. Ω	Temp.°C.	Res. Ω	Temp.°C.	Res. Ω
-85	10656K	-45	266.1K	- 5	20.71K
-84	9531K	-44	246.8K	- 4	19.63K
-83	8535K	-43	229.0K	- 3	18.62K
-82	7652K	-42	212.7K	- 2	17.67K
-81	6868K	-41	197.6K	- 1	16.77K
-80	6172K	-40	183.8K	0	15.93K
-79	5552K	-39	171.0K	1	15.14K
-78	5000K	-38	159.2K	2	14.39K
-77	4508K	-37	148.3K	3	13.68K
-76	4068K	-36	138.3K	4	13.02K
-75	3676K	-35	129.0K	5	12.39K
-74	3324K	-34	120.4K	6	11.80K
-73	3009K	-33	112.5K	7	11.24K
-72	2727K	-32	105.1K	8	10.71K
-71	2474K	-31	98.27K	9	10.21K
-70	2246K	-30	91.94K	10	9734
-69	2041K	-29	86.07K	11	9287
-68	1857K	-28	80.62K	12	8863
-67	1691K	-27	75.56K	13	8463
-66	1541K	-26	70.86K	14	8083
-65	1406K	-25	66.48K	15	7723
-64	1284K	-24	62.41K	16	7383
-63	1173K	-23	58.63K	17	7060
-62	1073K	-22	55.10K	18	6753
-61	982.2K	-21	51.81K	19	6462
-60	899.9K	-20	48.74K	20	6186
-59	825.2K	-19	45.88K	21	5924
-58	757.3K	-18	43.21K	22	5675
-57	695.6K	-17	40.71K	23	5439
-56	639.4K	-16	38.38K	24	5214
-55	588.1K	-15	36.20K	25	5000
-54	541.5K	-14	34.16K	26	4797
-53	498.9K	-13	32.25K	27	4603
-52	460.0K	-12	30.46K	28	4419
-51	424.5K	-11	28.79K	29	4244
-50	392.0K	-10	27.22K	30	4077
-49	362.3K	- 9	25.75K		
-48	335.0K	- 8	24.36K		
-47	310.1K	- 7	23.07K		
-46	287.1K	- 6	21.85K		

11. Thermistor Variance Before Adjustment

Thermistor resistance data at 25°C were examined to estimate variances between wafers and within wafers prior to adjustment. The purpose of the calculations was to estimate the per cent acceptable thermistors if adjustment is by-passed and wafers are cut to get the specified average resistance.

Wafers are cut into thermistors that are about 15% larger than the size desired. The thermistors are then individually adjusted to give the specified resistance by grinding. This process insures no losses.

Data on the average thermistor resistance from 22 wafers from seven rods were examined (Table 29) to see how closely the target value could be hit. The standard deviation was ±7.7% of the target value, with some evidence of bias in the square, N-type devices. Next the variation of the thermistors within a wafer was examined. Three wafers, producing 47 thermistors each, gave a standard deviation of ±4.5% around the wafer average. Therefore, the standard deviation for the thermistors around the target value was ± 9.0%.

If the process were changed to set the target value at the final desired resistance, some of the thermistors would be too small and would have to be discarded. With a standard deviation of ± 9 %, 17.5% of the thermistors would fall within ± 2 % of the target value   41.3% would be too small and 41.3% would be too large. If a ± 1.0% limit is set, only 8.8% would be acceptable and 45.6% would be out of limits on each side.

If the target value were lowered slightly from the objective to cut losses, the percent acceptable would drop also, but at a slower rate. An economic optimum exists and can be calculated if costs can be assigned to an unadjusted thermistor and to the adjustment process.

TABLE 29

WAFER TARGET RESISTANCE AND AVERAGE OBTAINED AT 25°C.

Circular

Target	Average Obtained	Rod C-189-15B P-Type	%Deviation from target
3480	3947	"	+ 13.42
3080	3147	"	+ 2.18
3200	3302	"	+ 3.19
3510	3785	"	+ 7.83
3580	3233	"	− 9.69
		Rod C-189-15B P-Type	
4050	4238	"	4.64
4050	4111	"	1.51
4130	4051	"	− 1.91
		Rod C-247-10 P-Type	
499	474	"	− 5.01
447	418	"	− 6.49
499	480	"	− 3.81
467	480	"	+ 2.78

Square

Target	Average Obtained	Rod C-189-15B P-Type	%Deviation from target
3450	3868	"	+ 12.12
3390	3700	"	+ 9.14
		Rod C-1177 N-Type	
179,000	164,000	"	− 8.38
180,000	160,000	"	− 11.11
		Rod C-3253A N-Type	
463,000	451,000	"	− 2.59
464,000	459,000	"	− 1.08
		Rod 3253 N-Type	
449,000	417,000	"	− 7.13
450,000	389,000	"	− 13.56
448,000	420,000	"	− 6.25
470,000	415,000	"	− 11.70

MINIMUM COST CONDITIONS

The acceptable thermistor unit cost is:

Cost of thermistors + cost to adjust

Final total of acceptable thermistors

OR:

$$C_U = \frac{100\ C_T + N_L\ C_A}{N_L + N_A}$$

WHERE:

C_T = Cost of unadjusted thermistor, \$/thermistor

C_A = Cost of adjusting, \$/thermistor

C_U = Product unit cost

N_L = % of thermistors too large and requiring adjustment

N_A = % of acceptable thermistors (not requiring adjustment)

N_S = % of thermistors too small

$$100 = N_L + N_A + N_S$$

The unit cost will be a mininum when:

$$-\frac{dN_L}{dN_S} = \frac{(100\ \frac{C_T}{C_A} + N_L)}{(N_L + N_A)}$$

This means for a given thermistor to adjustment cost (C_T/C_A) ratio, the optimum target resistance below specifications can be calculated. The results are shown on graph 16 for a $\pm$ 2.0% specification.

In the case of the thermistors produced under the contract it is very unlikely that the cost of adjustment C_A, (estimated at 15¢/device) is greater than the cost of a thermistor. Hence C_T/C_A would be greater than 1. Under these circumstances it would be desirable to cut the thermistors such that the target resistance is 14 to 15% below specs. The target resistance could be even farther below specs, but generally it is desirable to remove as little material as necessary in adjusting.

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TABLE 30

THERMISTOR SIZE DISTRIBUTION FROM CUTTING WAFERS AT VARIOUS TARGETS.

(Target values at and below resistance specification. Distribution
standard deviation ± 9 %, specification limits ± 2%.)

Target, % below specification resistance	THERMISTOR SIZE DISTRIBUTION, %		
	Too Small N_S	Too Large N_L	Within spec. N_A
0	41.3	41.3	17.4
1	37.1	45.6	17.3
2	33.0	50.0	17.0
3	29.0	54.4	16.6
4	25.2	58.7	16.1
5	21.9	62.9	15.2
6	18.7	67.0	14.3
7	15.9	71.0	13.1
8	13.4	74.8	11.8
9	11.1	78.1	10.8
10	9.1	81.3	9.6
12	5.3	86.6	8.1
14	3.4	90.9	5.7
16	2.3	94.7	3.0
18	1.3	96.6	2.1

12. Yields

Yields to be expected by using the manufacturing methods described are summarized in the block diagram (Figure 21). Notice that the yields when producing samples similar to those of the contract were approximately 85% based on the thermistor dice. We feel this figure can be considerably improved by operating a continuous balanced pilot line.

Included are estimated data for devices of half the diameter and thickness of the contract samples. Notice that at only 70% yield the number of thermistors obtained per unit of silicon is 3 to 4 times that obtained with the contract sample sizes. The problem of course is that size adjusting to within ± 1% is very difficult on the smaller samples. Perhaps improvements could be made to the size adjustment step so that these small sizes could be adjusted efficiently. In any case this seems to be the desirable direction in which to move in terms of quickness of response and yields.

SILICON ROD 8" LONG ⅞"-1" DIA.
WT. 215 gm.

7" OF GOLD DOPED
SILICON MONOCRYSTAL

68 WAFERS 2.0mm THICKNESS

3,740 THERMISTOR DICE
2.5 m.m. DIA. x 2.0 m.m.
(SIMILAR TO CONTRACT SAMPLES:
4,000 - 5,000 OHMS P-TYPE)

3,179 FINISHED THERMISTORS IN
±2% SPECS. APPROXIMATE 85% YIELD ON
THERMISTOR DICE.
~5% LOST SOLDERING
~5% LOST ADJUSTING SIZE
~5% REJECTED IN FINAL TESTS
YIELD BASED ON ACTUAL PILOT LINE OPERATIONS

110 WAFERS 1.0mm THICKNESS

4,950 THERMISTOR DICE
2.0m.m. x 2.0m.m. x 1.0m.m.
(SIMILAR TO CONTRACT SAMPLES:
N-TYPE 500,000 OHMS)

4,207 FINISHED THERMISTORS IN
±2% SPECS. APPROXIMATE 85% YIELD ON
THERMISTOR DICE.
~5% LOST SOLDERING
~5% LOST ADJUSTING SIZE
~5% REJECTED IN FINAL TESTS
YIELD BASED ON ACTUAL PILOT LINE OPERATIONS

160 WAFERS .5mm THICKNESS

20,000 THERMISTOR DICE
1.25m.m. DIA. x .5m.m.

14,560 FINISHED THERMISTORS IN
±2% SPECS. ESTIMATED 70% YIELD ON
THERMISTOR DICE.
~10% LOST SOLDERING
~10% LOST ADJUSTING SIZE
~10% REJECTED IN FINAL TESTS

13. Fitting of Experimental Points by Empirical Equation

As mentioned previously, the curves for both P- and N-type gold-doped silicon can deviate from a straight line on a logarithm of resistivity versus reciprocal of the absolute temperature plot. This deviation is greater in the case of P-type silicon, becoming significant at 25 or 30°C. At higher temperatures the curve flattens out such that at 200°C there is little sensitivity to temperature. However, there is still some sensitivity to temperature at say 100°C. We felt that if the experimental points could be fitted by a carefully selected empirical equation, it would extend the predictable portion of the curve. Hence the thermistors might be useable to 100°C, admittedly with some loss of sensitivity.

Equations for the resistivity as a function of temperature have been derived for gold-doped silicon. These have the general form:

$$R = B_1 T^F + B_2 e^{\Delta E / KT}$$

where:

R = resistance in ohms

B_1 = a constant

B_2 = a constant

F = a constant

ΔE = a constant

T = absolute temperature in °K

K = Boltzman constant

The experimental data were processed through a computer to find the values of the constants which gave the best fit or smallest standard deviation. In the case of the P-type silicon studied the best fit was obtained when, $E = 0.340$ e.v. and $F = 0$. The data are summarized in Table 31.

TABLE 31

Temperature (°C)	Experimentally Determined Resistance	Resistance Calculated $R = B_1 + B_2e^{\Delta E/KT}$
-58.56	79,600	80,016
-50.80	42,250	42,087
-40.49	19,200	19,157
-30.91	9,926	9,807
-20.38	5,052	4,993
-10.81	2,872	2,842
.00	1,600	1,587
+ 9.92	980.0	973.8
+19.99	620.5	620.4
+30.00	411.7	414.0
+40.00	285.6	288.7
+50.03	207.5	210.1
+60.18	157.0	159.1
+70.47	124.5	125.4
+79.98	104.2	104.2
+90.35	88.5	88.4
+99.99	78.0	78.0

Standard deviation, σ, = 0.8%

$B_1 = 45.85$
$B_2 = 8.069 \times 10^{-4}$

The fit of the data is very good. In only a few cases do the calculated points vary more than 1% from the observed points. The value of $\Delta E = 0.340$ agrees well with the values determined by independent techniques[13].

The reason for deviation from a linear log ρ vs. 1/T plot appears to be due to the saturation of the gold levels at high temperatures. The value of the empirical equation is that it allows the expression of resistance and sensitivity in an explicit manner at temperatures up to 100°C for P-type silicon. It also establishes the gold donor level precisely at 0.340 e.v. above the valence band.

14. Time Constant of Response

A study was completed comparing the time constant of response of our thermistors uncoated and coated with various materials to that of the Bendix AMT-4, ML419 radiosonde thermistor. Our thermistors measured 4 x 4 x 1 mm. The gold-doped silicon radiosonde thermistor is on the order of 2 x 2 x 1mm, hence the time constant would be somewhat less than in the case of this study. The time constant was measured while changing the temperature of the thermistor from 0°C to approximatley 26°C. The time constant was taken as the time in seconds for the resistance to change 63% of the total in an air stream of 800 ft/min. A summary of the results of this study is given in the table.

TABLE 32

Time Constant of Response

Sample No.	Nature of Coat	Time Constant (seconds)
1176	Uncoated	2.0
1180	Hand painted with 1 coat of white silicone enamel.	2.8
1182	Dipped in thinned(~25% in toluene) RTV-731* and then RTV-521**	3.9
1187	Hand painted with RTV-731 thinned at 50% with toluene	4.3
1186	Hand painted with RTV-731 thinned at 50% with toluene	4.6
1179	Dipped in thinned white silicone enamel	5.3
Bendix, AMT-4,ML419	Unknown	5.5
1178	Dipped in white silicone enamel, then hand painted with white silicone enamel to cover corners	7.2
1184	Dipped in RTV-731 thinned at 50%	7
1185	Dipped in RTV-731 thinned at 50%	7

 * - RTV-731 Dow Corning room temperature vulcanizing rubber.
** - RTV-521 Dow Corning room temperature vulcanizing rubber.

In order to obtain a desirable time constant it is necessary to keep the coating as thin as possible. The silicone enamel is desirable since a thin coating can be applied and it has high opacity. The coating which has the best temperature range is a Dow Corning room temperature vulcanizing rubber, RTV-731. Main problem with this material is that it is very viscous and difficult to apply in a thin coating. The hiding is not as desirable. We attempted to obtain thinner and more opaque coats by adding pigments and thinning with solvents such as xylene. This investigation was not successful because of the tendency of RTV-731 to polymerize when exposed to atmospheric moisture. Hand painting is the best technique for applying these coatings since dipping or spraying tends to leave the corners or edges of the thermistor deficient in paint. Based on the results of the study it was decided to use two hand-painted coats of silicone enamel on each thermistor with a baking period of about one hour at 200°C after the first coat and two hours after the second coat.

Information received later from the U. S. Weather Bureau pointed out that they define the time constant as "the time required for the thermistor to indicate 63% of the total increment in temperature in a stream of air with a speed of 820 ft/min." The increment can be positive or negative and the result should be about the same. The factor measured in this test is the physical ability of the thermistor to accept or dispose of heat to the environment.

To measure the time constant a small wind tunnel was made with two air intakes whose temperature and speed could be independently regulated. The temperatures used were 25°C and -10°C for testing the P-type material and the Bendix AMT-4,ML-419 thermistor; for the N-type thermistor 90°C and 25°C. The speed of the air was kept constant at 820 ft/min.

Ten readings were taken from each sample. For a given thermistor or a group of thermistors of the same kind, the maximum variation in the measurement was 4 tenths of a second.

The following table summarizes the results:

TABLE 33

Thermistor Number	Size in mm.	Ohms at 25°C	Time Constant in seconds Minimum (1)	Time Constant in seconds Maximum (1)
2m-3-7	2.5 dia. x 2.5	4K	2.0	2.2
W5-35	2.6 dia. x 2.6	4K	2.1	2.4
W2-34	2.6 dia. x 2.3	4K	2.1	2.2
3253-A-10	2.2 x 2.2 x 2.0	500K	2.1	2.4
3253-A-14	2.2 x 2.3 x 2.2	500K	2.1	2.4
3253-A-16	2.3 x 2.3 x 2.3	500K	2.3	2.5
2m-2-11	2.5 dia. x 3.0	5K	2.9	3.1
2M-2-21	2.5 dia. x 2.9	5K	2.9	3.3
2M-3-15	2.5 dia. x 2.9	5K	3.1	3.3
W-14-8	3.7 dia. x 1.9	.5K	2.9	3.2
Bendix M1-419	.7 dia. x 39	50K	3.1	3.4
W-15-4	3.8 x 3.8 x 2.3	.5K	4.2	4.5
W-6-12	7.8 x 3.8 x 2.5	.5K	4.7	5.1

(1) - Average of ten readings.

This table shows that the time constant of our thermistors, except the bulky 3.8 x 3.8 x 2.3 mm size, is equal or better than the time constant of the Bendix thermistor and well within the specifications of 5 seconds of the present contract.

15. Dissipation Constant

The dissipation constant is defined as the amount of power in milli-watts that has to be applied to a thermistor to raise the temperature of the thermistor one degree centigrade above the surrounding medium. For surrounding medium, manufacturers specify well stirred oil baths and still air. Both values are given with the characterization chart of the thermistor.

To measure the dissipation constant of the thermistors in still air, we use a cardboard box with a capacity of about 25 liters. The thermistors were evenly distributed hanging from the top of the box by their own leads. The box was sealed. Then the resistance of all the thermistors was measured using a current through the sample of 5 microamps. The resistance was remeasured increasing the amount of current. This step was repeated until the resistance of every thermistor showed a decrease equivalent to one degree centigrade or more. The measurements in oil were made using Dow-Corning 200-20 silicone oil stirring at constant speed and at 25°C. Again several measurements were taken increasing the current through the thermistor before each measurement until the resistance showed a decrease equivalent to 1° centigrade or more.

With the values obtained in the previous tests we were able to draw a smooth curve for each thermistor and find the exact value of the current that will give the difference of 1° centigrade higher than the surrounding medium. Having the current "I" and the resistance "R" of the thermistor, the power in milliwatts was calculated using the formula: $W = I^2R$. The following table summarizes the results.

TABLE 34

Thermistor Number	Size in mm.	Ohms at 25°C	Dissipation Factor in still air (milliwatt/°C)	in a well stirred oil bath (milliwatt/°C)
W- 6-12	3.8 x 3.8 x 2.5	0.5K	3.7	54
W-14-8	3.7 dia. x 1.9	0.5K	2.6	37
W-15-4	3.8 x 3.8 x 2.3	0.5K	2.6	-
2mm-3-15	2.5 dia. x 2.9	5K	2.8	52
2mm-2-11	2.5 dia. x 3.0	5K	2.8	60
W-5-35	2.6 dia x 2.6	4K	2.2	35
W-2-34	2.6 dia x 2.3	4K	2.1	35
2mm-3-7	2.5 dia x 2.5	4K	1.9	37
Bendix MI-419	0.7 dia. x 39	50K	0.8	1.5
I-27	2.2 x 2.2 x 2.2	500K	0.4	8
I-22	2.2 x 2.3 x 2.2	500K	0.4	8
A-14	2.2 x 2.3 x 2.2	500K	0.4	7

This table shows first, a fairly good reproducibility for thermistors of the same size and range; second, that the dissipation constant for the same thermistor is about 20 times higher in the oil bath than it is in air; and third, that all our thermistors excepting perhaps the high resist-ance, small size, N-type, have a higher dissipation constant than the Bendix thermistor.

16. Static Temperature Lifetime

Besides the data that have already been mentioned in previous sections on thermal stability, there are additional data to demonstrate the stability of single-crystal silicon thermistors when held for extended periods of time at a given temperature within the operating range. It is felt that the most severe conditions are those that occur at the upper end of the suggested operating range of 200°C. Any thermistor which is stable at 200°C would be stable at any temperature below 200°C. The table below summarizes aging data at 200°C for various types of thermistors both in the wafer size and in the diced form.

TABLE 35

Thermistor Stability

Thermistor No.	Type	Original Resistance (Ohms)	Hours at 200°C	Resistance After Treatment at 200°C
1	N	7305	1765	7302
2	N	7345	1765	7345
3	N	5688	1765	5685
4	N	5641	1765	5636
5	P	19.1	2199	18.8
6	P	22.1	2199	22.0
7	P	19.2	2199	19.1
8	P	18.6	2199	18.6
9	N	10,490	2816	10,150
10	N	12,230	2816	12,090
11	N	12,650	2816	12,460
12	P	635	4934	633
13	P	611	4934	615
14	P	614	4934	614
15	P	606	4934	603
16	P	610	4934	608

These data demonstrate that both the P- and N-type thermistor material are stable for extended periods of time, on the order of several thousand hours at temperatures in the range of 200°C. Frequently the change in resistivity is little or less than 1%.

III CONCLUSIONS AND RECOMMENDATIONS

Single-crystal semiconductor silicon, because of its purity, resistivity, energy gap, and availability, is an outstanding candidate for monocrystalline thermistor development.

Gold-doped monocrystalline silicon can produce thermistors which are highly reproducible, predictable and sensitive over the range of -85° to +200°C.

Float-zone leveling produces a product with less variability than diffusion material.

Forming of ohmic and mechanically sound contacts to gold-doped silicon results in good thermistor stability.

Measurement precision and speed are improved by the use of the comparison or ratio technique.

Final size adjustment is necessary to obtain high yields of devices with ±2% specifications.

Size adjustment on small thermistors is difficult.

The dependence of thermistor resistivity on resistivity of the starting silicon is very useful for production purposes.

Short-term annealing at 210°C can increase the temperature stability of gold-doped silicon.

Yields of 85% or better are possible when using the prescribed 28-step process for P-type silicon and 24-step process for N-type silicon.

Future work should be directed toward smaller-sized thermistors with very fast response times.

Size adjusting should be improved or revised so that it can be used on very small samples.

Other techniques of encapsulation such as canning should be investigated.

IV <u>BIBLIOGRAPHY</u>

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    1168, 1957.

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    p 3-1, McGraw-Hill Book Co., Inc., 1956.

13. Ibid., Collins, Carlson, and Gallagher, p. 1168.

V APPENDIX

W. R. GRACE & CO.

RESEARCH DIVISION

Washington Research Center, Clarksville, Maryland

TO: Dr. Wayne T. Barrett

FROM: Blanche B. White

DATE: October 3, 1961

SUBJECT: THERMISTORS - LITERATURE SEARCH LS - 46

In searching the literature for information on thermistor element properties and thermistor element fabrication, the following sources were consulted:

1. Applied Science and Technology Index 1947 - September 1961, and Industrial Arts Index.
2. Ceramic Abstracts 1945 - August 1961.
3. Chemical Abstracts 1907 - September 1961.
4. Engineering Index 1945 - 1960.
5. Monthly Index of Russian Accessions 1959 - September 1961.
6. Nuclear Science Abstracts 1948 - September 1961.
7. Physics Abstracts 1947 - September 1961.
8. Semiconductor Abstracts 1953 - 1958.
9. Solid State Abstracts and Semiconductor Electronics 1957 - 1961.
10. Technical Abstract Bulletin 1959 - September 1961.
11. U.S. Government Research Reports, Bibliography of Technical Reports, etc. 1946 - September 1961.

In addition, at our request, Astia prepared a bibliography, covering the last five years, of all documents in their collection pertinent to this subject. This was supplemented by a visit to Astia to search their older catalogue cards for any information in this field.

Information obtained from manufacturers concerning thermistors manufactured by them is listed in a section of the appended bibliography (p. 50-53).

The greater part of the rather extensive literature on thermistors covers the composition, method of manufacture, and properties of the various ceramic mixed oxide thermistors. Most frequently used of the oxides are Ni, Mn, Ti, Fe, Co, Cu and Cr. Oxides of Zn, Mg, Al, Li, Ta, V, Tb, U, Cb, Ba, Pb, Pr and Nb etc. are also mentioned in the patent literature.

Only two references were found to the use of III-V intermetallics in thermistors, and only a very limited number of references were found to the use of Si and Ge. Other semiconductor materials used for this application were also noted and references will be found in the bibliography.

There are numerous references describing specific applications of thermistors. These have not been included in the bibliography; however, a table showing general areas of application is included (p. 55).

Blanche B. White

Index General

Index to Abstracts

Thermistors

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   REVIEW OF THERMISTOR THERMOMETRY.
   AD-153,609, Sept. 1957.
   (Astia Bibliography).

   The usefulness of a thermistor as a thermometer is related to the
   following characteristics: (a) Sensitivity, (b) Time constant,
   (c) Ruggedness, (d) Reliability or stability.

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   TEMPERATURE-DEPENDENCE OF THE ELECTRIC CONDUCTIVITY OF THE Cu_2O-Ni_2O_3
   SYSTEM.
   Doklady L'vov Politekh. Inst. 1 (2), 13-18 (1955); Referat. Zhur., Khim.
   1957, No. 262.
   (C.A. 52, 13342i).

   The temperature dependence of the conductivity σ of samples obtained by
   sintering a mixture of 25% Ni_2O_3 and 75% Cu_2O was investigated. The
   linear function of $\log\sigma = f(1/T)$ shows 2 breaks at 140 and 230°. The
   energy of activation in the region below 140° is 0.7 e.v.; in the region
   140-230°, 0.907 e.v.; and in the region 230-300°, 1.106 e.v. The
   material is suggested for use in the construction of thermistors.

3. Aoki, Ikuo (Chiba Univ.).
   ELECTRICAL CONDUCTIVITY OF SEMICONDUCTORS; OXIDES OF COBALT AND MANGANESE.
   Ōyō Butsuri (J. Appl. Phys.) 21, 312-14 (1952).
   (C.A. 47, 3070f).

   Specimens were prepared by mixing oxides of Co and Mn in various ratios
   and sintering the mixtures at 1200°. The specific resistance R and the
   temperature coefficient dR/dT were measured at room temperature with the
   aid of x-ray powder photography. A minimum of R was found at the mole
   ratio Co:Mn = 2:1. The analysis of the diffraction rings shows that
   the specimen (I) having this mole ratio has the spinel structure (Mn,Co)-
   (Co,Mn)$_2$O$_4$. I has a comparatively high dR/dT. The specimen consisting
   only of Co_3O_4 and CoO has larger R and smaller dR/dT than does the mix-
   ture of Co and Mn. As Mn content increases, R increases rapidly. I may
   be the best for a stable thermistor with low R and high dR/dT.

4. Aoki, I.
   ELECTRIC CONDUCTIVITY OF MIXTURES OF OXIDES OF COBALT, MANGANESE, AND
   NICKEL.
   J. Coll. Arts and Sci. Chiba Univ. 1, 133-8 (1953); cf. C.A. 47, 3070f.
   (C.A. 49, 6681i).

   The structure of thermistors of the composition $Co_xMn_yO_z$ was determined
   by x-ray powder photography: Co_3O_4 + CoO for the ratio x:y = 1:0,
   Co_3O_4 + CoO + (Co,Mn) (Mn,Co)$_2$O$_4$ for the ratios between 8:1 and 2:1,
   (Co,Mn) (Mn,Co)$_2$O$_4$ for 3:2 to 1:1, (Co,Mn) (Mn,Co)$_2$O$_4$ + Mn_3O_4 for 4:5
   to 1:8, and Mn_3O_4 for 0:1. The composition of the system $Co_xNi_yO_z$ was

NiO for O:1, (Ni,Co)O for the ratios between 1:8 and 3:2, and (Ni,Co)O +
CoO + Co_3O_4 for 2:1 to 8:1. That of the system $Ni_xMn_yO_z$ was $NiMn_2O_4$ +
Mn_3O_4 for the ratio 1:3. $NiMn_2O_4$ for 1:2, $NiMn_2O_4$ + NiO for the ratio
between 1:1 and 3:1. Specific resistance vs. composition curves of the
Co-Mn-O system gave a minimum when x:y was equal to 2:1, and the activa-
tion energy of electric conductivity increased with Mn content. Specific
resistance of Co-Ni-O system gave a minimum when x:y was between 3:2 and
5:4, and the activation energy was minimum at x:y = 1:1. Specific re-
sistance of the Ni-Mn-O system was minimum at the composition $NiMn_2O_4$,
and the activation energy was minimum at the same composition. These
results suggest that the electric conductivity of Co-Mn-O and Ni-Mn-O
thermistors is explained by the inverse spinel structure, and the electric
conductivity of the Co-Ni-O system is attributed to impurity atoms present
in the NiO lattice.

5. Armour Research Foundation.
    PHYSICAL MECHANISM OF INFRARED DETECTORS.
    AD-121,051, March 10, 1956 - Oct. 31, 1956.
    (Astia Bibliography).

    A research program is in progress to illuminate fundamental conduction
    mechanism of thermistors. Questions posed are: (1) What are the atoms
    involved and how are they arranged? (2) How did this arrangement come
    into being? (3) How does the arrangement lead to certain mechanisms
    of electronic motion? and (4) How do these mechanisms give rise to the
    observed properties? The first two questions are answered by x-ray
    studies of Mn, Co and Ni oxides. Efforts are directed toward the third
    question, by determining valence states of cations in the lattics. This
    is done by (a) examining electrical properties of thermistor materials
    in which normal ratio of cations is varied, and (2) examining by neutron
    diffraction techniques thermistor materials in which relative propor-
    tions of Mn, Co, and Ni have been grossly altered.

6. Aso, Susumu, Sho Onuki, and Hiroshi Nishizawa (Nippon Elec. Co., Ltd.,
    Tokyo).
    THERMISTORS. I. TiO_2-Cr_2O_3 ROD-TYPE THERMISTORS.
    J. Electrochem. Soc. Japan 19, 145-8 (1951).
    (C.A. 45, 8923b).

    The manufacturing method is: sintering the mixture of TiO_2 and Cr_2O_3
    in 1:3 molar ratio at 1300° for 1 hour, and heating in H_2 at 1000° for
    1 hour. The electrical characteristics of the thermistors obtained are
    given. In spite of many disadvantages, the thermistors of this type
    could be applied to carrier and repeater telephone systems.

7. Aso, Susumu, Sho Onuki, and Hiroshi Nishizawa.
    THERMISTORS. II. TITANIUM DIOXIDE-CHROMIUM SESQUIOXIDE BEAD-TYPE
    THERMISTORS.
    J. Electrochem. Soc. Japan 19, 230-2 (1951); cf. C.A. 45, 8923b.
    (C.A. 46, 1367d).

    To obtain side-heater-type thermistors, the elements of the thermistor
    were improved to small-bead type (diameter = 0.4 mm.) having a small
    heat content. They were made by heating a mixture of TiO_2 and Cr_2O_3

(1:3 molar ratio) at 1300° for 30 minutes in vacuo. The bead-type
thermistors were superior in power sensitivity:rod type 22kΩ (0 mw.),
10kΩ (40 mw.). Several characteristics of side-heater-type thermistors,
thus prepared, together with the resistance variation owing to aging at
200° were observed. III. NICKEL MONOXIDE-MANGANESE OXIDE-COBALT OXIDE
THERMISTORS. Ibid. 295-6. $NiO-Mn_3O_4-Co_3O_4$ thermistors of higher γ
(resistance compressibility of side-heater-type thermistor) were pre-
pared by heat treatment in air. Resistance of the thermistors thus
prepared were 10kΩ-2meg.Ω. The constant B, in the equation $\rho=\rho_\circ$ exp.
(-B/T), was about 4500, and γ was 4.5-5.5. These results should be
compared with those of the $TiO_2-Cr_2O_3$ thermistors: B = approximately
2500, γ = 4.0 4.5.

8. Atkins, Robert M. (Atkins Technical Inc.).
    TEMPERATURE MEASUREMENT WITH THERMISTORS.
    Instruments and Control Systems 33, 86-88 (1960).

    The advantages of thermistors for temperature measurement applications,
    bases for probe selection, and future developments are outlined.

9. Atkins, P.A., and R.A. Setterington.
    THERMISTORS-APPLICATION IN TEMPERATURE MEASUREMENT AND CONTROL.
    Instr. Practice, Automation and Electronics 13 (10), 1042-7 (1959).
    (Ceramic Abstracts 1960, 43b).

    A review. 8 figures, 14 references.

10. Atkins Technical, Inc.
    ELECTRONIC THERMOMETERS.
    Semiconductor Electronics 3, No. 3898, (1959).

    The Thermophil electronic thermometer which utilizes germanium thermistors
    to measure surface and immersed temperatures between -200 and 450° is
    announced...

11. Automatic Telephone and Electric Co., Ltd., and Philip N. Roseby.
    TEMPERATURE-VARIABLE RESISTORS.
    Brit. 494,516, Oct. 26, 1938.
    (C.A. 33, 2823⁸).

    A resistance having a large negative temperature coefficient comprises
    a fused mixture of CuO and MnO_2. A mixture of CuO 75 and MnO_2 25% is
    fused in an arc between Cu electrodes, terminal wires being inserted
    in the melt and a globule of resistance material withdrawn and solidi-
    fied with the wires in position.

12. Bailey, H.T.
    THERMISTOR BASICS.
    Plant Eng. 13, 114-15, Aug. 1959.
    (App. Science and Techn. Index 1959, 410).

13. Baker, H. Dean, E.A. Ryder, and N.H. Baker.
    RESISTANCE THERMOMETER - SEMICONDUCTING SENSITIVE ELEMENTS.
    Temperature Measurement in Engineering. Vol. II. N.Y., Wiley [c1961].
    p. 5-8.

14. Barnes Engineering Co.
    THERMISTOR INFRA RED DETECTORS. PART 1. PROPERTIES AND DEVELOPMENT.
    AD-160,106 (1952-58), April 30, 1958.
    (Astia Bibliography).

    Barnes Engineering Co. under license from Western Electric started in
    1952 to manufacture thermistor infrared detectors utilizing the tech-
    nique developed at Bell Laboratories.
    Employed as infrared radiation detectors, thermistor elements are made
    small and thin and attached to a good heat sink to produce fast response.
    They are known as "solid-backed" thermistor infrared detectors or bolo-
    meters. Thermistor materials are metallic oxides, chiefly MnO, NiO,
    and CoO. They have a negative coefficient of resistance about 4%/°C.
    Materials used had resistance (ohm cm.) 2500 and 250 respectively,
    material constant ρ (°K) 3800 and 3400 respectively, and temperature
    coefficient of resistance $\alpha = -\frac{\rho}{R^2}$ .042° and .038° respectively (T = 30°K.).
    When a pulse of radiant energy $\angle w/$ falls on the blackened thermistor
    element, a portion is absorbed (about 60%) and heats the thermistor; at
    the same time heat generated in the thermistor is conducted away to the
    backing block.

15. Battelle Memorial Inst., Columbus, Ohio.
    TEMPERATURE ELEMENTS (THERMISTORS) COVERING THE PRODUCTS OF THE FOLLOWING
    MANUFACTURERS WW, XX, YY, AND ZZ.
    Report on Task 11 of Component Evaluation and Specification Engineering
    Test Data, Vol. 1, 1954, 214 p. including illustrations; AD-96,541.
    (Astia Bibliography).

    Battelle Memorial Inst., Columbus, Ohio.
    TEMPERATURE ELEMENTS (THERMISTORS) COVERING THE PRODUCTS OF THE FOLLOWING
    MANUFACTURERS WW, XX, YY, AND ZZ.
    Report on Task 11 of Component Evaluation and Specification Engineering
    Test Data, Vol. 2, 1954, 225 p. including illustrations; AD-96,542.
    (Astia Bibliography).

    Battelle Memorial Inst., Columbus, Ohio.
    TEMPERATURE ELEMENTS (THERMISTORS) COVERING THE PRODUCTS OF THE FOLLOWING
    MANUFACTURERS WW, XX, YY, AND ZZ.
    Report on Task 11 of Component Evaluation and Specification Engineering
    Test Data, Vol. 3, 1954, 72 p. including illustrations; AD-96,543.

16. Beakley, W.R.
    DESIGN OF THERMISTOR THERMOMETERS WITH LINEAR CALIBRATION.
    J. Sci. Instr. 28, 176-9 (1951).
    (Physics Abstracts 54, No. 6180 (1951)).

    Under certain circuit conditions a current or voltage may be obtained
    which varies almost exactly linearly with the temperature of a thermistor.
    Equations are given from which may be calculated: (a) the extent of the
    range of temperature within which departure from linearity is less than
    a specified value; (b) the circuit conditions which provide optimum
    linearity; (c) the sensitivity of the circuit in terms of current change
    per unit temperature; (d) the maximum permissible current through the
    thermistor.

17. Beck, A. (Australian National Univ., Canberra).
     STABILITY OF THERMISTORS.
     J. Sci. Instr. 33, 16-18 (1956).
     (C.A. 50, 69021).

     Thermistors may reach a state when their constants remain stable, however,
     they may undergo sudden arbitrary changes. This is probably due to sub-
     jecting the thermistors to temperatures outside the allowable range.
     Within certain limits, it is still possible to obtain temperatures accur-
     ate to within 0.02°.

18. Becker, Joseph A., and Howard Christensen (to Bell Telephone Laboratories
     Inc.).
     HIGH-TEMPERATURE COEFFICIENT RESISTOR.
     U.S. 2,633,521, Mar. 31, 1953.
     (C.A. 47, 6798b).

     A rapid-response temperature-sensitive resistor can be made having
     electrodes fired simultaneously with the semiconductive body. Thermis-
     tors of this type are free from noise, have increased power capacity
     and thermal response, and have lower resistance. The finely divided
     metal for the electrode (I) is mixed with a temporary binder (II) and
     spread in a thin film on a surface. Over this is spread a film of
     finely divided semiconducting material (III), with a high resistance
     temperature coefficient, with a temporary binder (IV). This double
     film is removed and heat-treated at 200-600° to remove II and IV and
     later fused at high temperatures. Another I may be applied to III in
     film form prior to the fusing operation. Alternatively, there may be
     interposed between each I film and III layer, films of mixtures of I
     and III. Finely divided Pt is used as I film to minimize the barrier
     layer at the I-III interface. III is comprised of one or more of MnO,
     NiO, CoO, Cu_2O, FeO, and ZnO. II and IV are methacrylates, vinyl
     polymers, or cellulose acetate butyrate with a volatile solvent. The
     thickness of the finished flake is on the order of 20 μ with 1 μ thick-
     ness for each electrode. The fusing temperature is 1100° for most
     oxides and not over 1450°.

*19. Becker, J.A., C.B. Green, and G.L. Pearson.
     PROPERTIES AND USES OF THERMISTORS - THERMALLY SENSITIVE RESISTORS.
     Elec. Eng. 65 (11) Nov. 1946 (Trans.) p. 711-25.
     (Eng. Index 1946, 370).

     New circuit element and control device is made of solid semiconducting
     materials whose resistance decreases about 4% per degree C.

20. Bemski, G., and J.D. Strenthers (Bell Telephone Laboratories).
     GOLD IN SILICON.
     J. Electrochem. Soc. 105, 588-91 (1958).
     (C.A. 52, 19488b).

     Heat-treatment of Si, both p-type and n-type, to temperature in excess
     of 900° frequently results in a decrease of lifetime and is sometimes
     accompanied by an increase in resistivity. In the present experiments
     it was found that Au was introduced during such heat-treatments in con-
     centrations sufficient to account for the observed changes in the

electrical characteristics. Au has been observed on the surfaces of all the Si samples examined so far. Heat-treatments in the temperature range 1100-1300° result in a concentration of Au in the bulk material of about 10^{14} at./cc. A film of Ni or Cu on the Si surface during the heat-treatment has a gettering action for Au. Heat-treatment in vacuo can also be effective in the removal of Au.

21. Benedict, R.P. (Westinghouse Elec. Corp., E. Pittsburgh, Pa.).
THERMISTORS VS. THERMOCOUPLES FOR TEMPERATURE MEASUREMENTS.
Elec. Mfg. 54 (2), 120-5 (1954).
(C.A. 48, 13287a).

Comparative tests of the thermoelectric properties of Fe-constantan thermocouple and a Thermistor (Victory Engineering Corp. Type 51A1) show greater sensitivity, higher stability up to 580° F., and shorter thermal time lag for the Thermistor...

22. Benson, G.W. (National Research Council of Canada).
USE OF THERMISTORS IN PRECISION THERMOMETRY.
AD-114,931, Oct. 22, 1956.
(Astia Bibliography).

Experiments were performed which indicate that the present manufacturing techniques will produce thermistors which are capable of being used as precision thermometers. Thermistors will allow temperatures to be measured with an accuracy approaching 0.001°C and appear to be stable over long periods of time. Thermistors can be made into practically any size or shape. Bead thermistors can be manufactured in extremely small sizes (down to 0.015 cm.). Small flake-type thermistors can be made with thermal relaxation times of the order of a few milliseconds and are suitable for handling rapidly changing temperatures. The nonlinearity of the thermistor makes precision calibration involved and the interpretation of the data obtained more difficult. The upper limit of the temperature range of thermistors is controlled by their thermal instability. This can be expected to improve with improved manufacturing techniques. It is probably unwise to use them much above 150°C without extensive preliminary tests of higher temperature stability. The low-temperature limit arises as a result of their extreme sensitivity. At low temperatures, their resistance increases so much that the measuring circuit, which is designed for the higher temperature range, becomes insensitive. Circuits can be specially designed for these low-temperature regions.

23. Bol, Arie (to Hartford National Bank and Trust Co.).
     ELECTRICAL RESISTOR.
     U.S. 2,608,633, Aug. 26, 1952.
     (C.A. 47, 983c).

     In the manufacture of electrical resistors, in which the resistance
     element consists of a sintered homogeneous spinel phase of Fe_3O_4
     and Zn_2TiO_4 in a 1:1 ratio, the conducting leads are attached by cement-
     ing them into the ends of the element. The leads are inserted in holes
     at the ends of the element, an aqueous paste of 45% Ag_2O and 55% Fe
     powder is then applied in the holes. The element is heated at 600°
     for about 2 minutes to cause the Ag_2O and Fe to react exothermically
     and form a mixture of Fe_3O_4 and Ag, which is liquid at the high tem-
     perature of the reaction. If the conducting leads have a very smooth
     surface, a small amount of low-melting glass can be used as a flux
     in the adhesive mixture. Ti powder can be substituted for the Fe powder.

24. Bol, Arie, Christiaan A.M. Klaasen, and Pieter J.W. Jochems (to North
     American Philips Co., Inc.).
     NEGATIVE-TEMPERATURE-COEFFICIENT ELECTRICAL RESISTORS.
     U.S. 2,863,840, Dec. 9, 1958.
     (C.A. 53, 8896i).

     Electrical resistors with negative temperature coefficient are made
     by sintering a mixture of powdered oxides or carbonates of Ni and Li
     at 1100-1300°. The electrical uniformity varies with the trace element
     content of the Ni source, but this variation may be suppressed by
     incorporation of 1-30 (preferably 10-20) mole % CuO into the sintered
     mass. For example, powdered NiO and CuO were ground for 16 hours with
     alcohol in a ball mill with addition of an amount of $LiCO_3$ sufficient
     to give final proportions of 15 and 1.5 mole % CuO and LiO_3 respectively,
     the rest being NiO. To 100 grams of the filtered, dry mixture, 5 grams
     of a binder solution containing 20 grams Me acrylate and 1 ml. di-Bu
     phthalate per 100 ml. MeOAc was added. The resulting mass was molded
     into 5 X 5 X 15-mm. rods and sintered at 1240° for 1 hour. Extensive
     data are given to show the improvement of electrical uniformity result-
     ing from the inclusion of CuO.

25. Bosson, G., F. Gutmann, and L.M. Simmons.
     A RELATIONSHIP BETWEEN RESISTANCE AND TEMPERATURE OF THERMISTORS.
     J. Applied Phys. 21, 1267-8 (1950).
     (C.A. 45, 18871).

     The equation $R = A + B/(T + \Theta)$ for the resistance R of a thermistor at
     T° K. is proposed. Least squares analyses of the most precise resistance-
     temperature data available for 3 different thermistor materials show
     that the equation is a considerable improvement over its predecessors...

26. Brackenbury, P.S.
     RESEARCH AND DEVELOPMENT OF SEMI-CONDUCTING MATERIALS. PRACTICAL
     APPLICATIONS FOR ULTRA-SENSITIVE TEMPERATURE MEASURING EQUIPMENT AND
     AUTOMATIC CONTROL AND STABILIZING PROBLEMS. INTERROGATION OF ERWIN WEISE.
     BIOS Final Report 1658, Feb. 1946.
     (Bibliography of Scientific and Industrial Reports 9, 892 (1948).)

     The semi-conductors in which Weise had carried out research were in a
     material known as magnesium titanium spinel (MgO · TiO$_2$) bearing the
     trade name of Urdox. This material is made in the form of sheet, rod,
     and tube. It is also possible to make them in the form of fine fila-
     ments of about 70 microns diameter formed on a thread of silk of about
     30 microns. Method of manufacture, list of publications by Weise or
     in collaboration, and patents made by Weise are given as well as
     remarks to uses and possible use.

27. The British Thomson-Houston Co., Ltd.
     RESISTANCES.
     Brit. 496,210, Nov. 21, 1938.
     (C.A. 33, 2823^7).

     A resistance having a substantially linear negative coefficient of
     resistance from 0$^\infty$ to 50° consists of Te, alloyed or not with Ag,
     formed in single crystals by progressive solidification from a molten
     state and annealed at 105-25° for a time depending on the annealing
     temperature and the coefficient required.

28. Broom, R.F.
     A LOW-TEMPERATURE RESISTANCE THERMOMETER USING p-TYPE GALLIUM ARSENIDE.
     J. Sci. Instr. 35, 467-8 (1958).
     (Physics Abstracts 62, No. 3402 (1959)).

     The construction and calibration of the thermometer are described.
     The thermometer consisted of a single crystal of copper-doped gallium
     arsenide with copper-plated contacts. The resistivity of the thermo-
     meter material was 2.5 X 10^5 ohm-cm. at 4.2° K. and the sensitivity,
     defined as TR^{-1} (dR/dT), was approximately constant at 2.5 over the
     range 2 to 25° K. The thermometer was photoconductive and must be
     screened from light for reliable readings.

29. Brophy, J.J., N. Rostoker, and L.V. Azaroff (Armour Research Foundation).
     SEMICONDUCTING PROPERTIES OF IRON OXIDE THERMISTOR MATERIAL.
     Phys. Rev. 98, 228 (1954).
     (C.A. 50, 10511a).

     The semiconducting properties of iron oxide thermistor material containing
     10% each of copper and titanium ions as impurities have been examined.
     This material, prepared by sintering the oxide powder, is found to have
     the crystal structure of alpha Fe$_2$O$_3$ indicating simple substitution of
     copper and titanium for iron ions in the lattice. The resistivity is a
     logarithmatic function of temperature having an activation energy of 0.52
     electron volt. Hall effect and Seebeck effect studies of the semicon-
     ductor show that this variation is due to thermal activation of carriers
     to conduction levels. The carriers are found to be electrons with

mobility of about 1.0 cm^2/volt second. Concurrent with the origin of
electrical conduction is ferromagnetic behavior, and a saturation mag-
netic moment of 2.0 emu/gram at room temperature is observed above
magnetic saturation at about 5000 oersteds. A discrepancy between donor
concentration determined from extrapolated carrier density measurements
and the known concentration of impurity atoms appears to indicate a type
of cancellation between the effect of copper and titanium atoms.

30. Brouwer, G.P.
    THERMISTORS.
    Ned. Tijkschr. Natuurk 19, 149-58 (1953).
    (C.A. 48, 9237d).

    A review dealing with properties and uses of semiconductors of high
    negative temperature coefficient.

31. Burkin, A.L., and I.T. Sheftel'.
    COBALT-MANGANESE OXIDE SEMICONDUCTOR BOLOMETERS.
    Fiz. tverdogo Tela, 2 (2), 288-96 (1960).
    (Physics Abstracts 63, No. 8836 (1960)).

    The basic parameters characterizing the performance of thermistor
    bolometers are defined and classified, and 3 methods are given for their
    measurement. The construction of 3 types of bolometer is discussed in
    detail and their performance is described.

32. Burkin, A.L., O.N. Filippova, and I.T. Sheftel'.
    KMT-14 THERMISTOR.
    Elektrichestvo No. 5, 71-3 (1960).
    (Monthly Index of Russian Accessions 13, 3018 (1960)).

33. Chapin, W.E., and P.G. Perry.
    TEMPERATURE ELEMENTS, THERMISTORS.
    AD-96,820, June 15, 1954.
    (Astia Bibliography).

    The electrical performance was investigated of rod, disk, and bead
    thermistors as affected by low-temperature storage, moisture resistance,
    temperature cycling, shelf life, and continuous-load life. The program
    also included an investigation of temperature hysteresis and steady-
    state-current time characteristics of galvanic action, terminal and body
    strength, and the effects of soldering on the terminals. Specimens used
    were purchased from 4 specified manufacturers (WW, XX, YY, and ZZ as
    indicated in the manufacturers' code which was previously transmitted
    to the Signal Corps Engineering Laboratory). The values of material
    constants (β) for the scheduled specimens were calculated from the
    initial measurements and varied between 1400 and 4600. Stable thermal
    characteristics were noted in the specimens. Resistance changes under
    increasing and decreasing temperature were normally between the limits
    of 0.12 and 2.0%. Very slight changes in β were noted as a result of
    temperature-cycling, cold-storage, and shelf-life and load-life opera-
    tions. Moisture-resistance exposure resulted in average changes up to
    2% in β, and the presence of galvanic action was noted in 1 of 24 types
    of elements. Negative resistance values are graphed. The spread of the
    current-voltage characteristics among the 10 specimens comprising a

group of the same make, type, and resistance was very narrow. Strength
tests applied to the terminals of the specimens provided a wide range
of results from 1 ounce to 15 pounds. The changes in resistance as a
result of terminal soldering were consistent and very small. Terminal-
twist tests indicated that all terminal leads can be expected to fail
in a range between 1 and 5 twists.

34. Christensen, Howard, and Joseph J. Kleimack (to Bell Telephone Labs, Inc.).
    METALLIC-OXIDE RESISTOR.
    U.S. 2,462,162, Feb. 22, 1949.
    (C.A. 43, 4403a).

    In making resistors of sintered metallic oxides, the oxides are permitted
    to come to equilibrium with an O-containing atmosphere at the temperature
    at which the equilibrium O content of the body is such that the desired
    resistance is obtained, and then the resistor is sealed off from the
    surrounding atmosphere.

35. Christensen, Howard (to Bell Telephone Labs, Inc.).
    THERMISTOR BY OXIDATION OF A NICKEL-MANGANESE ALLOY.
    U.S. 2,636,012, April 21, 1953.
    (C.A. 47, 7700d).

    Thin, thermally sensitive conductive flakes suitable for use as thermis-
    tors (thermally sensitive resistive elements) are prepared from thin
    foils of an alloy containing 80 atomic % Mn and 20 atomic % Ni. The
    foils, which have a thickness of 0.5-25μ, are heated in an oxidizing
    atmosphere to 600-700° and kept in the furnace for at least 16 hours,
    during which time the temperature is allowed to drop to 450-500°. The
    alloy is completely oxidized by this treatment without separation of
    the two oxides. To produce a spinel-type crystalline structure, the
    oxidized material is heated from 450-500° to 875-1150° in 2 hours.
    The final product consists of smooth-surfaced flakes, a relatively
    uniform mixture of Ni and Mn oxides. It has stable electrical pro-
    perties and is relatively free from mechanical irregularities. The
    starting material may contain 40-90 atomic % Mn and 10-60 atomic % Ni.

36. Christensen, Howard (to Bell Telephone Labs, Inc.).
    HIGH-TEMPERATURE-COEFFICIENT RESISTORS.
    U.S. 2,674,583, April 6, 1954.
    (C.A. 48, 11683h).

    Thin-film resistors whose resistance varies greatly with temperature
    are formed by first mixing a long-chain-polymer temporary binder with
    particles of resistor material of such dimensions relative to the length
    of the polymer chain that a gel mixture forms. Resistor particles of a
    larger size are then added to the mixture. They are held in suspension
    by the gel, thereby providing a film of uniform density. In a typical
    example, the resistor flakes are composed of Mn and Ni oxides combined
    in an Mn:Ni atomic ratio of 2-4:1. In preparing a mixture for resistor
    flakes, 6 grams of a thermistor material having a particle size of 0.5-
    1μ is milled with 6 grams of a temporary binder and 12 cc. of solvent
    in a high-speed ball mill to about 1% of the original particle size in
    6 hours. An additional 7 grams of resistor material (2μ) is added to
    the mixture, which is then milled an additional hour. A thin film of

this mixture is spread on a smooth, flat surface to a thickness of several μ. The film is dried, removed from the flat surface, and cut into the desired sizes and shapes. The binder is removed from the un-cured flakes by heating to 400°. The temperature is then raised to 1000-300° in about an hour, cooled gradually to 860°, and cured for 16 hours at this temperature. After cooling, electrodes are attached to the flakes. As binders, isobutyl methacrylate and cellulose acetate butyrate can be used.

37. Clark, Layton E., Jr.
   DETERMINATION OF EXACTNESS OF FIT OF WESTERN ELECTRIC TYPE 14B THERMISTOR
   TO THE EQUATION LOG R = A + $\frac{B}{T+\theta}$ AND LOG R = A + $\frac{B}{T+\theta}$ + CT.
   AD-156,261, Feb. 26, 1958.
   (Astia Bibliography).

   The closeness of fit of tht two formulas over the -65 to +50° C. tem-perature range was tested against the calibration of 47 Western Electric Type 14B thermistors, comprising samples for four production lots. Both formulas describe semiconductors of the Western Electric Type 14B within an accuracy of +0.1° C., except below -55° C. where a correction to the formula must be applied. The four-constant equation describes the 14B thermistor with inaccuracies not greater than +0.04° C. with no correc-tion to the formula at temperatures above -55° C., and within ±0.04° C. below -55° C. if corrections are made to the formula.

38. Clark, Layton E.
   REPORT ON DETERMINATION OF EXACTNESS OF FIT OF THERMISTORS TO THE
   EQUATIONS LOG R = A + $\frac{B}{T+\theta}$ AND LOG R = A + $\frac{B}{T+\theta}$ + CT.
   AD-251,845, Jan. 1961.
   (Astia Bibliography).

   The exactness of fit of the equations Log R = A + B/(T + θ) and Log R = A + B/(T + θ) + CT has been tested on a well-diversified selection of rod, disk, and wafer thermistor types, over all or portions of the tem-perature range of -60° C. to +180° C. Data of these calibrations as well as tabulations of closeness of fit, expressed in temperature units, are presented in tabulated form for the convenience of those who may be considering a given thermistor type for use in a specific temperature-measurement application.

39. Coler, Myron A.
   ELECTRICALLY CONDUCTIVE PLASTIC MATERIALS.
   U.S. 2,761,849, Sept. 4, 1956.
   (C.A. 51, 768b).

   Plastic particles are coated with conductive compounds, e.g., Ag_2S, Fe_3O_4 or Cu_2O. Moldings exhibit electrical conductivity intermediate between that of metals and untreated plastics. The physical properties of the composition are substantially unchanged. Thus, 80 grams 20-mesh polystyrene beads and 20 grams Ag_2S (average nominal particle size 0.0005 inch) were ball milled 16 hours with steel balls, 90% of the sur-face of the beads being thus covered with Ag_2S. The particles were compression molded at 175° for 10 minutes at 10,000 pounds/sq. in. and cooled under pressure. The products had a specific resistance of 7 X 10^6 ohm-cm. at 20° and 4 X 10^6 ohm-cm. at 30°. They are useful in making thermistors.

40. Collins, C.B. (General Electric Co.).
    SILICON CURRENT CONTROLLING DEVICES.
    U.S. 2,871,330, Jan. 27, 1959.
    (Semiconductor Electronics 3 (1), No. 3687 (1959)).

    An iron-doped silicon thermistor which is highly sensitive to tem-
    perature changes in the range from about -100 to 100° C. and an iron-
    doped silicon photoconductive cell which is highly sensitive to radia-
    tion, particularly infrared radiation, in the temperature range 0 to
    -200° C. are described. The magnitude of the resistance of these
    devices over the temperature ranges is such that they are useful in
    electrical control circuits.

41. Compagnie générale d'électrocéramique S.A.
    ELECTRICALLY CONDUCTING CERAMIC COMPOSITION FOR RESISTANCES.
    Fr. 1,094,342, May 18, 1955.
    (C.A. 52, 20976a).

    In the manufacture of ceramic resistors, the scattering of the resis-
    tivity values caused by the varying degree of oxidation or reduction
    of the metal oxide in the furnace is eliminated by using compositions
    of clay containing Ti, Sn, or Ce as a plastifier and Si as an internal
    reducing agent. The necessity for controlling the atmosphere and (or)
    the addition of special additives is also avoided. The conductivity of
    such products increases with increasing Si content until a TiO_2:Si
    ratio of 3.85 is reached. Higher Si content has little effect. Pre-
    paration of the compositions and firing is done by the usual methods.
    The scattering of the resistivity is weakest when the conductivity is
    low and when the firing is done rapidly. The resistances thus obtained
    function normally at 800-900°. Typical compositions (TiO_2, Si, clay,
    and kaolin, respectively, in %) and their resistivities (r) at 20°,
    300°, and 800°, respectively, are: 52, 13.5, 21.5, 13, r = 4.6, 0.8,
    0.2; 44.3, 11.5, 27.4, 16.8, r = —, 4, 2.3; 36.3, 9.4, 34.4, 19.9,
    r = 110, 23, 9; 27.8, 7.25, 40.6, 24.35, r = 9000, 1500, —. The
    oxides of Sn and Ce behave similarly. Addition of these oxides to TiO_2
    modifies the temperature coefficient and the expansion coefficient.

42. Companie générale de télégraphie sans fil.
    ELECTRIC RESISTORS WITH HIGH NEGATIVE TEMPERATURE COEFFICIENT (THERMIS-
    TORS).
    Fr. 1,052,015, Jan. 20, 1954.
    (C.A. 52, 14397i).

    The thermistors described can be used at ambient temperatures and have
    permanent electrical characteristics reproducible within ± 5%. This is
    achieved by controlled processing and careful choice of metallic oxides.
    Processing consists of homogenization by milling of the oxides for 400
    hours with W carbide balls and by long mixing or precipitation of easily
    decomposed organic salts. Minor components can be introduced by im-
    pregnation of the powder with solutions of their salts. Compression to
    very high pressures and heating to >1000° follows. At least a portion
    of the metallic oxides belongs to groups with the same number of elec-
    tronic orbits, the same number of electrons in the outer-most orbit,
    but a variable number of electrons in the orbit immediately below.

For example, pure oxides are mixed in the proportions Mn_2O_3 78, NiO 14, and Fe_2O_3 4%. Then 2% Al_2O_3 and 2% SiO_2 are added. The mixture is processed as above and the 10-mm. pills obtained are covered with a Ag-base glaze and baked once more at a temperature higher than the one at which they are to be used. Connections are soldered on and the thermistor painted with a silicone-base varnish. Resistivity at 25° is 100,000 ohm-cm. and temperature coefficient at 25°, 0.053 ohm/ohm/°C.

43. Compagnie générale de télégraphie sans fil.
THERMISTORS.
Fr. Addition 65,137, Jan. 26, 1956. Second addition to Fr. 1,052,015
(C.A. 52, 14398a).
(C.A. 53, 22622b).

New compositions of metallic oxides provide improved reproducibility of resistivity and more lasting stability. The mixture consists of 3.5% Al_2O_3, a suitable amount of MnO_2 (at least 47%) and at least one of the oxides of Ni, Co, and Cu. Typical compositions are: (1) MnO_2 80-6%, Co_2O_3 0.5-15, and Al_2O_3 3.5-5%; (2) MnO_2 52-6, Co_2O_3 32-6, NiO 8-10, and Al_2O_3 3.5-5%; and (3) MnO_2 47-52, Co_2O_3 27.5-36, NiO 7-9, Al_2O_3 3.5-5, and CuO 10-12%. Resistivities were 50-150, and 90-150 kohm-cm./sq. cm., respectively. Cf. Fr. Addition 63,332.

44. Compagnie generale de telegraphie sans fil (by A. Vassiliev).
ELECTRIC RESISTORS.
Fr. 1,129,167, Jan. 16, 1957
(C.A. 54, 10604i).

Electric resistors are composed of metal oxide ions in an amount of Mn 75-95, Ni 4-25, and Cu 1-10%, based upon MnO_2, NiO, and $CuCO_3$-$Cu(OH)_2$. The oxide mixture is ball milled, presintered at 600-1100°, and ground. To the resulting frit, up to 15% of clay is added. The mixture is fired, ground, mixed with an organic binder, such as starch, and extruded. The final firing takes place at 1200° for 2 hours. Within the indicated composition range, values of ρ may be varied between 50 ohm-cm. and 100,000 ohm-cm., and the coefficient B between 2800 and 4300. In the equation $\rho = \rho\infty.e^{B/T}$, ρ is the resistance at 25°, $\rho\infty$ is the resistance at a very high temperature, and T is the temperature in degrees Kelvin. It is shown that, with the ratio MnO_2:NiO constant, ρ is a function of the amount of CuO present and can thus be predetermined. The addition of clay has several important advantages. It has a stabilizing effect upon the changes of ρ occurring with aging. This is explained by the assumption that during the heating of MnO_2, lower oxides, such as Mn_2O_3 or Mn_3O_4, are produced which subsequently undergo reoxidation. The latter is inhibited by the glassy phase formed by clay around the oxide particles. Clay also improves the values of ρ and B and renders firing conditions, such as control of temperature and rate of heating, less critical. By promoting better cohesion during extrusion, the addition of clay also permits the shaping of units of >10 mm. in diameter.

45. Compagnie industrielle des céramiques électroniques (Humbert and Masson, inventors).
    THERMISTOR MATERIALS.
    Fr. 1,112,965, Mar. 21, 1956.
    (C.A. 53, 8574e).

    Substances having a negative temperature coefficient of resistance for thermistors that resist high energies (>2 w.) are manufactured by mixing 80-97% of a powdered thermistor material obtained by known methods, e.g., as in Fr. 1,052,015 (C.A. 52, 14398a) and Fr. 1,052,361, with 3-20% V_2O_5, shaping the mixture with an organic binder under pressure, and heating the article at 600-700°. Thus, a mixture of powdered MnO_2 560, NiO 90, CoO 350, and Al_2O_3 40 grams was agglomerated with 100 grams urea and sintered for 24 hours at 1200°. The thermistor obtained was crushed, screened through 60-mesh, mixed with 115 grams V_2O_5, shaped at 1 ton/sq. cm. with 60 grams ceresin as a binder, and fired a second time at 700° for 1 hour.

46. Council of Scientific and Industrial Research.
    CERAMIC CONDUCTING BODIES.
    Indian 53,608, Jan. 18, 1956.
    (C.A. 50, 9709e).

    Anatase-type TiO_2 is wetted with H_2O, granulated to 20-mesh, and dried to 10% moisture. It is then pressed into wafers or rods, dried at 100° for 24 hours, and stacked over blocks of ZrO_2 and separated by ZrO_2 granules. The temperature of the oven is raised in 3 stages: overnight to about 900°, 1 day to 1200°, and 8 hours at 1380-450°. The semiconductors thus obtained may be used as thermistors up to 1000° for rectification or amplification.

47. Counts, William E., Robert W. Smith, and Karl Schwartzwalder (to General Motors Corp.).
    CERAMIC SEMICONDUCTOR COMPOSITIONS.
    U.S. 2,962,452, Nov. 29, 1960.

    A ceramic composition is formed of 15 to 60 TiO_2; 0 to 50 SnO_2; up to 15 Ta_2O_5, Nb_2O_5 or V_2O_5; 20 to 40 Al_2O_3, magnesia, millite, zircon, or chrome oxide; up to 10 parts MoO_3, WO_3, or mixtures thereof; and trace impurities, the Ta_2O_5, Nb_2O_5, and V_2O_5 being present in small but effective amounts to reduce the resistance to the desired value, and the MoO_3 and WO_3 being present in small but effective amounts to reduce the voltage coefficient of resistivity to the desired value.

48. Dearborn, Ernest F. (to Bell Telephone Labs, Inc.).
    ELECTRIC RESISTOR WITH NEGATIVE TEMPERATURE COEFFICIENT.
    U.S. 2,274,592, Feb. 24.
    (C.A. 36, 4237²).

    Oxides are used together, such as NiO 23, Mn_3O_4 47 and Co_2O_3 30%.

49. Doucet, Y.
     USE OF THERMISTORS.
     J. Phys. Radium 12, 823 (1951).
     (Physics Abstracts 55, No. 970 (1952)).

     Comments are given on thermistors. The best are the type "F" in which
     sporadic fluctuations limit the precision to about ± 0.002° C. The
     curve log RVf(1/T) is not linear, as suggested by theory...

50. Dul'nev, G.N., and V.P. Savinov.
     PRECISION OF TEMPERATURE MEASUREMENT BY SEMICONDUCTIVE THERMOSENSITIVE
     RESISTANCES.
     Issledovaniya v Oblasti Teplovykh Izmercnii (Moscow-Leningrad: Gosudarst.
     Nauch.-Tekh Izdatel. Mashinostroitel. Lit) Sbornik 1956, 150-8; Referat.
     Zhur., Khim. 1957. Abstract No. 12267.
     (C.A. 53, 11904h).

     The absolute temperature error is $\sigma = PxF$, where P is the dispersive
     power of the semiconductor thermosensitive resistance, and F is a co-
     efficient dependent on the construction of the resistance, on the
     thermal conductivity of the material, and on the operating conditions.
     The coefficient F can be determined theoretically for a series of
     simple semiconductive thermosensitive resistances.

51. Estermann, I., A. Foner, and J.A. Randall (Carnegie Institute of
     Technology).
     RESISTIVITY OF GERMANIUM AT LOW TEMPERATURES AND THE EFFECT OF ADDITIONS.
     Physical Reviews 71, 484 (1947).

     The resistivity ρ of several germanium samples was measured between room
     temperature and 13° K. The purest sample shows a very steep increase
     of resistivity with cooling at temperatures below 30° K. giving a linear
     relation between $\log\rho$ and 1/T. The samples with low impurity concentra-
     tion (both N and P type), e.g., 0.006 atmosphere percent Al, show a
     slight decrease in resistivity on cooling from room temperature to about
     150° K., followed by an increase to about 2½ times the minimum value at
     13° K. The sample with higher impurity concentration (0.04 atmosphere
     percent Al) shows practically no change in resistivity over the whole
     temperature range. In this sample, however, the resistivity at all
     temperatures increased substantially after the first four cooling and
     warming up operations; the same effect, but to a much lesser degree, was
     observed in other samples. Typical results are given in table below.

Sample	Type	273°K	180°K	Resistivity in ohm-cm. at 90°K	60°K	20°K	14°K	13°K
"pure"	—	17.5	19.2	11.2	9.2	73	1840	—
P added	N	0.0242	0.0234	0.0301	0.0384	0.0551	0.0560	0.0560
0.006 at % Al	P	0.0324	—	—	0.0330	0.0641	0.0723	0.0712
0.04 at % Al (first run)	P	0.00510	0.00472	0.00520	0.00585	—	—	—
0.04 at % Al (fourth run)	P	0.00937	—	0.0086	0.0086	0.0088	0.0087	0.0087

52. Estermann, I., A. Foner, and J.E. Zimmerman (Carnegie Institute of Technology).
RESISTIVITY OF GERMANIUM SAMPLES AT LIQUID HELIUM TEMPERATURES.
Physical Reviews 75, 163 (1949).

The resistivity of several germanium samples with different amounts of added impurities was measured between 4°K. and 20°K. Samples with high impurity content, in which the electron gas is degenerated below 100°K., do not change their resistivity in this temperature range. Another sample, which has a degeneracy temperature of 20°K., computed from Hall Effect measurements, showed the same behavior. Two other samples, which did not become degenerate above 20°K., exhibited a moderate increase in resistivity (20 and 80 percent respectively) between 20°K. and 4°K. Two "pure" samples, i.e., without added impurities, showed a very strong increase of resistivity below 20°K., increasing from about 2 ohm-cm. at 20°K. to more than 3 X 10^5 ohm-cm. at 4.7°K. At these low temperatures, however, the resistance depends strongly on the applied electric field, and this effect requires further study.

53. Fenwal, Inc., Ashland, Mass.
HIGH TEMPERATURE THERMISTORS.
AD-228,572, July 1, 1959 - Sept. 30, 1959.
(Astia Bibliography).

Beads are made by daubing a discrete quantity of a suitably prepared mixture on a pair of parallel wires. The wire is strung onto a frame which allows for adjustment of the wire tension and spacing. The beads are fired 4 hours at 2700°F. Three mixes were used: Mix A.— 6.3 grams Cr_2O_3, 1.85 cc. $Cr(NO_3)_3 \cdot 9H_2O$ solution (specific gravity 1.2), H_2O added; Mix B— To 5.0 grams Cr_2O_3, $Cr(NO_3)_3$ was added (specific gravity 1.2), and as mix dried more $Cr(NO_3)_3$ was added; Mix C— To 5.0 grams Cr_2O_3, $CuNO_3$ was added (specific gravity 1.2) and as the mix dried more $CuNO_3$ was added. Mix A is most promising. It is felt particle size plays a part in ease with which bead forms. Beads are tested at 77° and 200°F. for resistance. It is felt furnace used for firing is faulty leading to low bead resistance.

54. Fenwal, Inc., Ashland, Mass.
HIGH TEMPERATURE THERMISTORS.
AD-232,165, Oct. 1, 1959 - Dec. 31, 1959.
(Astia Bibliography).

The quantity of $Cr(NO_3)_3$ in the bead mix ($Cr_2O_3/Cr(NO_3)_3$) can be used to control the amount of spread in the resistance distribution of the fired beads. A small amount of densifier in the bead mix will increase the mean resistance and strength of the beads but may result in a cracked bead structure. Firing in the new furnace takes 18 minutes (in contrast to earlier 6 hours heating, 4 hours soaking and 6 hours cooling). The beads are well sintered and green in color. Bi_2O_3 was used as the densifier.

55. Fenwal, Inc., Ashland, Mass.
    HIGH TEMPERATURE THERMISTORS.
    AD-236,765, Jan. to March, 1960.
    (Astia Bibliography).

    This report is concerned with testing of stability of chromic oxide
    bead thermistors. The firing technique was studied as a cause of
    poor stability.

56. Fisher, Joseph R. (to Bell Telephone Labs, Inc.).
    ELECTRIC RESISTANCE ELEMENTS.
    U.S. 2,082,102, June 1.
    (C.A. 31, 4910^6).

    A method of producing resistors having a high negative temperature
    coefficient of resistance, for use in electric circuits, consists in
    placing a quantity of Ag sulfide powder between a pair of dies, apply-
    ing sufficient pressure to dies to compress the Ag sulfide powder
    into a coherent mass, removing the resistance from the lower die,
    heating it in an atmosphere of S vapor for approximately 1 hour at
    300-400° and then heating it in a stream of pure dry N at 200-300°
    for approximately 1 hour.

57. Fisher, Joseph R. (to Bell Telephone Labs, Inc.).
    ELECTRIC RESISTORS.
    U.S. 2,091,259, Aug. 31.
    (C.A. 31, 7344^3).

    Resistors having a high negative coefficient of resistance for use in
    electric circuits are produced by subjecting a mass composed substan-
    tially of pure Ag to S vapor heated to 300° until the mass is converted
    into Ag sulfide.

58. Foëx, M.
    CERAMIC BODIES FORMED FROM Al_2O_3 AND V_2O_3.
    Silicates ind. 17, 326-9 (1952).
    (C.A. 47, 1910e).

    V_2O_3 is, in many respects, different from Al_2O_3, comparable to the
    differences in the ionic constants of Al^{+++} and V^{+++}. Its powder can
    be pressed and sintered to compact bodies which have a high electric
    conductance (similar to graphite), and also a high thermal conductance,
    like corundum. The inversion at -100° is characterized by a great
    change in properties: the modification which is stable at lower tem-
    peratures is a good insulator. Mixed powders of Al_2O_3 and V_2O_3 have
    been pressed and sintered at 1450-1800° in an atmosphere of H. There
    are two series of crystalline solutions: (I) in the concentration
    range from 100 to 50 molecular % V_2O_3; (II) from 100 to 90 molecular %
    Al_2O_3. The products II are easily made from Al_2O_3 and V_2O_3 powder,
    the latter, after fusing, acting as a bond; V_2O_5 is reduced to V_2O_3
    in the subsequent sintering in H. With increasing Al_2O_3 content, the
    products I show decreasing elementary cell dimensions, but V_2O_3 is
    chemically stabilized by the Al_2O_3 addition. The crystalline solution

phases are highly refractory, with fusion points near 2000°, and an indistinct eutectic in the unmixing gap. The electric conductance of the bodies was measured in the range from -100 to +200°; the resistance, $\jmath$, is a function of temperature. A graph with log $\jmath$ plotted vs. molecular Al_2O_3 concentration shows two different systems of curves, for bodies fired at 1450° and at 1800°, with lower values for those fired at 1800°. Even a body with 95 molecular % Al_2O_3 fired at 1800°, is still a conductor, but with 1450° as the firing temperature the log $\jmath$ is above 7 in a sample with 70 molecular % Al_2O_3. The temperature coefficient of $\jmath$, as a function of the Al_2O_3 content, increases gradually over a wide range in composition, but above 90% Al_2O_3 it increases suddenly. Products fired at 1450° are friable, and oxidize slowly in air, while those fired at 1800° are stable, hard, and reproducible. Bodies of type II are useful as "thermistances," i.e., electric resistors sensitive to temperature changes, and with a negative temperature coefficient of $\jmath$. In this respect, they are similar to thermistances of magnetite, to which spinellides are added (e.g. Cr spinel). The thermal shock resistivity of the Al_2O_3-V_2O_3 bodies is satisfactory, their thermal expansion moderate, the thermal conductance high. Products II are hard, but still grindable. Theoretically, the hardness of corundum must be raised by the admixture of V^{+++} ions in the crystal structure. It is possible that Al_2O_3-V_2O_3 bodies may be used as electric heating elements, up to 1800°, either in massive bodies, or as surface-treated Al_2O_3 ceramics, with V_2O_3 introduced by diffusion. An addition of Cr_2O_3 to Al_2O_3-V_2O_3 bodies may increase the stability of V_2O_3 against atmospheric oxidation.

59. Friedberg, Simeon A. (Carnegie Institute of Technology).
     GERMANIUM-INDIUM ALLOYS AS LOW TEMPERATURE RESISTANCE THERMOMETERS.
     Physical Reviews 82, 764 (1951).

     A previous survey of semiconducting samples indicates that materials with about 2 X 10^{17} impurity centers/cm^3 and room temperature resistivities of about 0.05 ohm cm. should have large enough temperature coefficients of resistivity at liquid helium temperatures to make good secondary thermometers. Experiments on p-type samples cut from a melt of germanium and 0.001 atomic % indium are described. The influence of the original location of a sample in the melt on the magnitude and reproducibility of its change of resistivity with temperature is discussed. Satisfactory thermometers have been obtained from such a melt by surveying the resistivities between 4.2°K. and 1.6°K. of samples from slices taken perpendicular to the vertical axis. Strips from the uppermost layer of the melt are found to have about 1.5 X 10^{17} impurity centers/cm^3 and resistivities at 300°K. of about 0.08 ohm cm. From this group, a thermometer has been selected having a temperature coefficient of resistivity of -1 (degrees K.)$^{-1}$ at 4°K. and -370 (degrees K.)$^{-1}$ at 2°K. Its use in temperature measurement, reproducible to better than 0.01°K. throughout the helium range, is discussed.

60. Friedberg, S.A.
     SEMICONDUCTORS AS THERMOMETERS.
     American Institute of Physics. Temperature, Its Measurement and Control in Science and Industry. N.Y., Reinhold, 1955. Vol. II. p. 359-382.

61. Genser, Milton, and Worth B. Allred (Battelle Development Corp.).
SEMICONDUCTOR MATERIAL.
U.S. 2,816,023, Dec. 10, 1957.
(C.A. 52, 9789d; see also Semiconductor Abstracts VI, No. 1516 (1958)).

AlSb semiconductors are prepared by incorporating Ta in AlSb by treating Al and Sb in a Ta-lined container. The method produces semiconductor material having a resistivity of 10^3-10^6 ohm-cm., which can be used as thermistors, photoconductors, or infrared detectors. The semiconductor has a carrier concentration of 10^{12}-10^{13} carriers per cubic cm. and can be used in the band between 0.8 and 4μ.

*62. Gibson, W.T. (Standard Telephones and Cables, Ltd.).
THERMISTOR PRODUCTION.
Electrical Communication 30 (4), 263-70 (1953).

Methods of manufacture of bead, pellet, and rod type thermistors by Standard Telephones and Cables, Ltd., are described. Raw materials used are Ni, Mn and Cu oxides.

63. Gildart, Lee W.
SEMICONDUCTOR MATERIALS FOR THERMISTORS.
U.S. 2,837,618, June 3, 1958.
(C.A. 52, 14350d; see also Semiconductor Abstracts VI, No. 1515 (1958)).

A thermistor material is made from 96% by weight Sb_2S_3 and 4% As_2S_3, both of at least 99.9% purity, by heating to about 650° and then cooling. The resistivity of the resulting alloy is 140 ohm-cm. at 25°. An alloy containing 75% Sb_2S_3 and 25% As_2S_3 has a resistivity of about 12,000 ohm-cm. at 25°. These materials can be incorporated into thermometer probes by melting a granular form of the composition and allowing it to fuse around a pair of electrode tips.

64. Gizzi, A.J. (General Electric Co.).
THE GROWING THERMISTOR FIELD.
Electronic Design 6, 12-15 (April 30, 1958).
(Semiconductor Electronics 2, No. 2635 (1958)).

Present and future applications of thermistors are discussed and the results of a thermistor market survey are presented. The present limitations of thermistors are outlined.

65. Goodyear, Robert S.
THERMAL RESISTOR ELEMENTS FOR ELECTRICAL CIRCUIT APPLICATIONS.
Product Eng. 16, 93-5 (1945).
(C.A. 39, 2675⁴).

Graphs show characteristics and performance of thermal resistor elements formed from metallic oxides. These resistor elements, which consist of metallic oxides pressed into disks, extruded rods, or formed into tiny beads, can be used as small electric-circuit elements, resistance of which changes with temperature. Some thermistors are produced with resistance values ranging from a few ohms to several megohms. The temperature of a thermistor may be changed by external

heating, or by heating due to passage of electric current, or by a
separate heating coil in close contact with the thermistor element.
Static characteristics of a directly heated thermistor relating
voltage, current, resistance, and power are given. A directly heated
thermistor can be used as a time delay device. Resistance thermo-
meters, having a thermistor as the measuring element, are far more
accurate than are thermocouples. Thermistors in similar bridge cir-
cuits can be used as flow meters or vacuum gages, or wherever the
physical quantity to be measured can affect the flow of thermal energy
from a hot body. Externally heated thermistors can be used as variable-
resistance devices. Standard relays can be protected against high-
voltage surge in the circuit by placing a directly heated thermistor
in series with the winding.

66. Gould, Harold L.B., Burton A. Kingsbury, and Victor E. Legg (to Bell
     Telephone Labs, Inc.).
     ELECTRIC RESISTOR UNIT.
     U.S. 2,274,830, Mar. 3.
     (C.A. 36, 4036⁹).

     A stable, resistor unit of high negative resistance-temperature coeffi-
     cient comprises a self supporting plate of consolidated, finely divided,
     heat-treated resistance material, the major constituent of which is one
     or more of the oxides of Fe, Ni, and Co, the plate having a thickness
     less than approximately 1/12 of its smallest surface dimension, and
     being provided with contact means including at least one heat-distribut-
     ing member on opposite faces of the plate.

67. Gray, Truman S., and Marvin Van Dilla.
     THERMISTORS; THEIR CHARACTERISTICS, USES AND ASSOCIATED CIRCUITS.
     Bibliography of Scientific and Industries Reports 1, 280 (1946).

     The temperature-sensitive electrical resistor (thermistor) is a recent
     development of the Bell Telephone Laboratories. Its most important
     property is an unusually high temperature-resistance coefficient as
     compared to conventional temperature-sensitive wire. It is particularly
     useful in problems involving measurement and control of temperature and
     related quantities. Report contains descriptions of various models of
     thermistors, their uses and associated circuits. A parts and acces-
     sories list for thermistor electronic thermometer, illustrations, a
     chart and a diagram are included.

68. Groschwitz, E.
     ON THE THEORETICAL TEMPERATURE COEFFICIENTS OF SEMICONDUCTORS.
     Z. angew. Phys. 7 (5), 245-9 (1955).
     (Physics Abstracts 58, No. 7031 (1955)).

     The temperature coefficient of resistance of semiconductors is derived
     for materials of varying degrees of purity and for different tempera-
     ture ranges. The temperature effects of p-n junctions are determined
     from the diffusion currents of the minority carriers.

69. Haayman, Pieter, Arie Bol, Frans C. Romeyn, and Evert J. W. Verwey
    (to Hartford National Bank and Trust Co.).
    METHOD OF MANUFACTURING SEMICONDUCTIVE MATERIAL.
    U.S. 2,735,824, Feb. 21, 1956.
    (Ceramic Abstracts 1956, 119j).

    A resistor having a given value of specific resistance consists
    essentially of substantially homogeneous mixed crystals produced by
    heating a mixture of about 99 molecular % of ferric oxide and about
    1 molecular % of titanium dioxide in air at a temperature of about
    1200°.

*70. Hardy, L.H., and H.R. Emes (The Carborundum Co. Refractories Division,
    Perth Ambay, N.J.).
    THERMISTORS IN TRANSISTOR CIRCUITS.
    Semiconductor Products 3 (8), 31-35 (1960).
    (Eng. Index 1960, p. 1497).

    Temperature compensation of transistor circuits can be accomplished
    inexpensively and with relative simplicity through the use of negative
    temperature coefficient resistors, thermistors. Thermistors are
    available in a wide range of resistance values and temperature coeffi-
    cients. Time constants similar to transistor time constants are
    available. Characteristics of available thermistors are discussed
    together with methods for determination of characteristics and a
    description of how they should be specified. Some typical applications
    of thermistors in compensating transistor circuits are also discussed.
    Thermistors for temperature compensation are available in 3 basic
    types. All 3 are manufactured in a range of resistivities and tempera-
    ture coefficients. The highest coefficient (steepest slope) is that of
    cobalt-Mn-Ni oxide types which are available in disc, rod, and washer
    form. These types possess negative temperature coefficients of approxi-
    mately 3-5.2% per °C. Thermistors possessing intermediate slope are
    composed of Ti and Fe oxides and are available primarily in rod form.
    The negative temperature coefficient of these types can be from 1.3-
    2.5% per °C. The least change with temperature is that exhibited by
    the SiC types which are available in rod form and possess coefficients
    of 0.25-0.55 per °C. The resistance-temperature characteristic of a
    thermistor is specified by β value: $R_T = R_0 e^{\beta (\frac{1}{T} - \frac{1}{T_0})}$, where T_0 =
    reference temperature in °K., R_0 = resistance at T_0, T = temperature
    of thermistor in °K., R_T = resistance at temperature T, and β = beta
    value or resistance-temperature constant. Since the resistance-
    temperature characteristic of a thermistor is non-linear, β varies
    with temperature, generally increasing with temperature.

71. Inutuka, Hideo, and Syuziro Kawase (to General Electric Co.).
    SINTERED METALLIC COMPOSITIONS SUITABLE FOR TIME-DELAY RELAYING DEVICES.
    U.S. 2,294,755, Sept. 1.
    (C.A. 37, 863⁴).

    CuO 95-60 and FeO or chromic oxide 5-40% are used in forming a sintered
    composition which has a negative coefficient of resistance and which is
    substantially nonporous and free from change with respect to negative
    temperature coefficient of resistance after having been heated to high

temperatures. U.S. 2,294,756 relates to a process of manufacturing resistances, which involves mixing a powdered oxide of a metal such as Cr_2O_3 with one or more powdered metals such as Cu and shaping the mixture and sintering it at 1000-1300° in the presence of an oxidizing medium such as O to effect oxidation of the metal or metals.

72. Jonker, Gerard H., Gerard W. van Oosterhout, and Jan H. van Santen (to North American Philips Co., Inc.).
SINTERED ELECTRICAL RESISTORS.
U.S. 2,862,891, Dec. 2, 1958.
(C.A. 53, 6842f).

Resistors having a specific resistance range of 0.2-5750 ohm cm., and a temperature coefficient between -0.5 and -4.3%/°C. are described. The composition of these resistors corresponds approximately to $AB_nD_{1-n}O_3$ in which A is a mixture of at least 1 ion of the group La^{+++}, Nd^{+++}, and Pr^{+++} and at least 1 ion of the group Ca^{++}, Sr^{++}, Ba^{++}, and Pb^{++}; B is at least 1 ion of the group Fe^{+++}, Cr^{+++}, and Co^{+++}; D is at least one ion of the group Fe^{4+}, Cr^{4+}, Co^{4+}, and Mn^{4+}; and n is >0, but <1. Co^{3+} and Co^{4+} are present only when at least 1 of the other metal ions besides those represented by A in the above formula is present, the elements Co, Fe, and Cr being present in both the tri- and quadrivalent states. Resistors are claimed in which the conductive phase contains: (1) Co in an amount up to 90 atomic % of the total of Fe, Cr, Co, and Mn; and (2) Al, Ti, and (or) Ni in a total amount up to 20 atomic % of the total of Fe, Cr, Co, and Mn. Also claimed is a resistor containing up to 10% flux.

73. Kaganov, M.A.
DETERMINING CHARACTERISTICS OF THERMISTORS USED IN MEASURING EQUIPMENT.
Priborostoenie No. 3, 5-7 (1960).
(Monthly Index of Russian Accessions 13, 2084 (1960)).

74. Kamiyama, Masahide, and Ziro Nara (Univ. Tokyo).
PROPERTIES OF Mn_3O_4-NiO THERMISTORS.
Ôyô Butsuri 21, 400-2 (1952).
(C.A. 47, 8505h).

Seven samples of thermistors were prepared from MnO_2 and NiO by sintering the mixtures of various ratios at 1300° (3 hours) and annealing at 500° (24 hours). MnO_2 changed to Mn_3O_4 on sintering. The electric resistance R was measured at various temperatures to calculate the activation energy E, which is for samples of MnO_2:NiO ratio in weight, (1) 1:0 (pure Mn_3O_4), 0.48 e.v., (II) 4:1, 0.37, (III) 3:2, 0.33, (IV) 2:3, 0.36, (V) 1:4, 0.46, and (VI) 0:1 (pure NiO), 0.61. There is a minimum of E at 7:3 corresponding to a minimum of R. The thermoelectric-power measurements at temperature difference 5 ~ 6° showed that I, II, and IV were of p-type and III, IV, and V were of n-type. The 7:3 sample (VII) was of n-type below 200° and p-type above that temperature. X-ray powder photography showed that VII was composed of II and III and relative magnitude of R of II and III determined the type of VII. Mn_2NiO_4 is contained in every sample except I and VI, and plays an important role in these thermistors.

75. Kasperovich, A.S., and A.G. Shashkov.
    SEMICONDUCTOR THERMISTORS.
    Izv. vys. ucheb. zav. energ. 2 (6), 133-4 (1959).
    (Monthly Index of Russian Accessions 13, 316 (1960)).

    Review by N. P. Udalov of book of this title.

76. Kasperovich, A.S.
    METHODS FOR DETERMINING THE THERMAL CONSTANT OF TIME OF A THERMISTOR.
    Trudy Inst. energ. ANBSSR 6, 222-7 (1958).
    (Monthly Index of Russian Accessions 13, 680 (1960)).

*77. Keonjian, E., and J.S. Schaffner. (General Electric Co., Syracuse, N.Y.)
    SHAPING THE CHARACTERISTICS OF TEMPERATURE-SENSITIVE ELEMENTS.
    Communication and Electronics 1954, 396-400.

    A method for shaping the characteristics of temperature-sensitive ele-
    ments is described. The proposed method can be applied to any tempera-
    ture-sensitive element provided the coefficient of the temperature-
    sensitive element is larger than that of the desired characteristic
    and the characteristic of the temperature-sensitive element does not
    change with the applied voltage.

78. Kolomiets, B.T., and I.T. Sheftel.
    TEMPERATURE MEASUREMENT BY SEMICONDUCTOR RESISTANCE THERMOMETERS.
    J. Tech. Phys., U.S.S.R. 17, 1105-10 (1947).
    (Physics Abstracts 52, No. 1438 (1949)).

    Resistance-temperature characteristics are given for UO_2 over the range
    0-100°C. Thermistor resistance thermometer elements are described and
    rate of response demonstrated. Sensitivity and scale distribution are
    tabulated for various temperature ranges, obtained in conjunction with
    the usual circuit bridge.

79. Kolomiets, B.T. (Acad. Sci., U.S.S.R., Leningrad).
    HOT CONDUCTORS.
    Elektrichestvo 1947, No. 3, 20-7; Chem. Zentr. (Russian Zone Ed.)
    1948, II, 1158.
    (C.A. 44, 8801f).

    Methods of preparation are given for hot conductors (with a negative
    temperature coefficient) of the following materials and the properties
    of such conductors are discussed: U oxide (obtained by heating UO_2-
    $(NO_3)_2 \cdot xH_2O$ to 500°), CuO (from NaOH + $CuSO_4$ solution, heated to 90°),
    a mixture of Cu and Mn oxides (addition of NH_3 to a solution of $CuSO_4$
    and $MnSO_4$ at 80°), a mixture of Ti and Mg oxides, and Ag_2S (from $AgNO_3$+
    H_2S). The conductors were formed from the compressed powders, which
    were then heated for varying periods depending upon the resistance
    values. Electrical connections were made (except with the CuO con-
    ductor) by reduction of an applied Ag_2O solution. Tables are given
    which report the resistance values obtained, the relation between
    conductivity and temperature, and the manner in which this latter
    relation varies with the duration and temperature of calcination
    (minutes to hours and 500-1300°). Within a definite range the con-
    ductivity of the CuO-MnO conductor scarcely varied with the composition

of the mixture or with the temperature of calcination. At a
conductivity of 10^{-1} reciprocal ohms per cm. the temperature coeffi-
cient of this hot conductor corresponded to that of an ordinary hot
conductor at a conductivity of 10^{-3} to 10^{-4} reciprocal ohms per cm.
Other materials recommended as suitable for hot conductors were $CuOCrO_3$,
Mn_3O_4 + NiO, and PbSe.

80. Kunzler, J.E., T.H. Geballe, and G.W. Hull (Bell Telephone Labs,
     Murray Hill, N.J.).
     GERMANIUM RESISTANCE THERMOMETERS SUITABLE FOR LOW TEMPERATURE
     COLORIMETRY.
     Rev. Sci. Instr. 28, 96-8 (1957).

81. Lark-Horovitz, K., A.E. Middleton, E.P. Miller, and I. Walerstein
     (Purdue University).
     ELECTRICAL PROPERTIES OF GERMANIUM ALLOYS. I. ELECTRICAL CONDUCTIVITY
     AND HALL EFFECT.
     Physical Reviews 69, 258 (1946).

     Germanium samples purified by high vacuum treatment have been alloyed
     by adding from 0.001% to 1.0% of metallic impurities. The electrical
     conductivity and transverse Hall effect of these samples have been
     investigated over temperatures ranging from -180°C. to 650°C. Plotting
     log ρ (resistivity) and log R. (Hall constant) against 1/T shows that
     the resistivity at low temperatures decreases with increasing tempera-
     ture, increases around room temperature and then drops sharply with a
     slope identical for the various samples. The Hall curves indicate
     electron (N type) or hole (P type) conduction, depending upon the type
     of impurity. P type samples show reversal of Hall effect, and the
     slope at high temperatures is identical for all samples, P and N alike,
     indicating that germanium behaves at low temperatures as an impurity
     semiconductor, but is at high temperatures an intrinsic semiconductor
     with energy level separation of about 0.76 volt. Hall values show
     that the number of current carriers ranges from about 10^{13} up to 10^{19}
     per cc. The temperature behavior of mobility, determined by R/ρ,
     cannot be explained as due to lattice scattering alone, but indicates
     the existence of another scattering mechanism, especially at low
     temperatures.

82. Lark-Horovitz, and V.A. Johnson (Purdue University).
     THEORY OF RESISTIVITY IN GERMANIUM ALLOYS.
     Physical Reviews 69, 258 (1946).

     The temperature dependence of resistivity of germanium alloys is
     considered in three ranges: (1) the impurity range of low tempera-
     tures with conduction due to impurity electrons or holes, (2) the
     transition range with contributions from both impurity and intrinsic
     electrons and holes, and (3) the intrinsic range of temperatures so
     high that the numbers of electrons and holes are equal. Resistivity
     in the impurity range is the sum of resistivity due to lattice
     scattering (proportional to $T^{\frac{1}{2}}$) and resistivity due to impurity
     scattering. Mean-free-path calculations indicate that the impurity
     mean-free-path increases and the lattice mean-free-path decreases with
     rising temperature. At a given temperature the lattice mean-free-path

is the same for all germanium samples, but the impurity mean-free-
path varies widely with impurity content.

83. Loman, Geo. T. (to Bell Telephone Labs, Inc.).
     THERMISTORS.
     U.S. 2,694,050, Nov. 9, 1954.
     (C.A. 49, 2226d; Semiconductor Abstracts 3, No. 858 (1955)).

     Stable thermistors with a large temperature coefficient of resistance
     are made from combinations of oxides of Ni, Mn, and Fe in the system
     $NiMn_{3-4}$ oxide: $NiFe_{2-4}$ oxide by heating at about 1000° for 16 hours
     a typical mixture contains NiO 14.94, Fe_2O_3 15.97, and Mn_2O_3 15.79
     grams. The oxides are mixed in a colloid mill with distilled H_2O
     acidified with AcOH for better wetting. After filtering, the result-
     ing cake is dried and screened and a binder, e.g. 5 grams iso-Bu
     methacrylate/100 grams of oxides, is added together with a solvent,
     e.g. 1 gram xylene/gram of oxide. Dimethyl phthalate in a ratio of
     5 cc./100 grams of oxides can be added before a second screening to
     control the consistency of the mixture. Resistor bodies of the disk
     type are prepared from the screened cake by pressing approximately 1
     gram of material in a 1/2 inch diameter die at about 12,700 pounds/
     sq. inch. The pressed disks are heat treated in air at 500° for about
     4 hours to remove binder after individually burying each disk in a
     finely divided refractory, e.g. 120-mesh Alundum. Sintering takes
     place at 1000-1400° in 16 hours. Each face is covered with a layer
     of conductive material, e.g. a paste of finely divided Ag or Pt mixed
     with the above binder and cured at 600°.

84. Meyer-Hartwig, E., and H. Federspiel (Terlano, Italy).
     MANUFACTURE, REGULATING ACTION, AND APPLICATION OF ELECTRIC RESISTORS.
     Bull. assoc. suisse élec. 42, 135-42 (1951).
     (C.A. 45, 4628a).

     Resistance materials with negative temperature coefficients in which
     the current flow is due to electrons and not to ions, which with direct
     current cause decomposition, are described. The best materials for the
     manufacture of thermistors are oxides of U, Cu, Cr, Ni, Mn, and mixed
     oxides with a spinel basis, and products on a metalloceramic basis of
     a special composition. The maximum temperature of operation is for
     pure U oxide in a protective tube at 600°, pure Cu oxide at 220° in
     air, mixed oxides of Cr, Ni, Mn, Co at 300° in a protective tube and
     at 150° in air, spinels (Mn, Ti) 500° in a protective tube, and for
     capillary thermistors, i.e., mixtures of metals and nonmetallic sub-
     stances, 600° in a protective tube and 450° in air. Methods of manu-
     facture, properties, current control, and fields of application are
     described. Fifteen references.

85. Misener, A.D., and L.G.D. Thompson.
     PRESSURE COEFFICIENT OF RESISTANCE OF THERMISTORS.
     Canad. J. Techn. 30, 89-94 (1952).
     (Physics Abstracts 55, No. 6473 (1952)).

     The pressure coefficient of resistance for one type of thermistor
     thermometer was determined up to pressures of 2000 pounds per inch[3]

at temperatures of 0°, 25° and 50°. The pressure coefficient at any given pressure appeared to be independent of temperature but changed rapidly with pressure, decreasing with increased pressure from -3 X 10^{-6} per pound per sq. inch at atmospheric pressure to -1.5 X 10^{-6} per pound per inch^2 at 1000 pounds per inch^2 and approaching zero value at 2000 pounds per inch^2...

86. Miller, Wm. A. (to Radio Corp. of America).
     ELECTRIC RESISTORS.
     U.S. 2,511,216, June 13, 1950.
     (C.A. 44, 7682a).

     Resistors with negative temperature coefficient are made out of TiO_2, partially decomposed to Ti metal by vacuum firing near the melting point. Hard, blue-to-black colored ceramic bodies are obtained by compressing pure TiO_2, in vacuo, heating 1300-1640°, and later in an inert gas such as He, Ne, or A.

87. Miura, Senzo (Nippon Univ., Tokyo).
     THERMISTOR FILMS.
     Ôyô Butsuri 28, 117-19 (1959).
     (C.A. 53, 21195a).

     A thermistor film was obtained by evaporating a rod thermistor (baked mixture of Co_3O_4 and CuO and of Mn_3O_4 and NiO) onto a plate of fused quartz at 1500° and 10^{-5} mm. Hg and heat-treating in air (500-600°, 3-5 hours for the Co-Cu system and 250-350°, 3-5 hours for the Mn-Ni system). The temperature dependence of the electrical resistance of the films had the same trend as that   the original rod. Electron diffraction studies made after growing the particles in the film by sintering showed that the oxides had the spinel structure. The use of the films as infrared bolometers is suggested, their response being 0.07-0.12 volt (r.m.s.) per watt (at 15 cycles per second) and the time constant 0.05-0.09 second.

88. Morin, Francis J. (to Bell Telephone Labs, Inc.).
     SEMICONDUCTOR OF MIXED NICKEL, MANGANESE, AND IRON OXIDES.
     U.S. 2,645,700, July 14, 1953.
     (C.A. 47, 10384c).

     Thermistors covering a wide temperature range and with a reproducible temperature coefficient of resistance are manufactured from stable, spinel-type compounds, such as $NiMn_2O_x$ - $NiFe_2O_x$ or $NiMn_4O_x$ - $NiFe_4O_x$, which are mutually soluble in all proportions. The concentration of O varies with the partial pressure and sintering temperature. NiO 18.67, Mn_2O_3 19.73, and Fe_2O_3 19.96 grams (1μ particles) are mixed in a colloid mill with distilled H_2O and AcOH (or make slightly basic). After thorough mixing petroleum wax in triethanolamine is added; the binder is precipitated onto particles. The mixture is then filtered and pressed to the desired form, wax is evaporated at 300°, and the body is sintered in air at 1200° for 16 hours. The recommended atomic ratio for (Mn plus Fe)/Ni is 2-4; this gives a specific resistance of 3 X 10^3 to 2 X 10^7 ohm cm. at 25°; when the ratio is 2, the temperature-dependence factor is approximately 3500-4600°, while at 4, it is approximately 3700-5800°.

89. Murrell, T.A.
     FINAL REPORT ON THERMISTORS.
     AD-555,580, March 1, 1950.
     (Astia Bibliography).

     Three general types and shape factor are represented in the 205
     thermistors described: rods, discs, and threads. They were prepared
     in 18 different batches with varying heat treatments; the electrical
     properties varied over wide limits. The resistance at 25°C. ran from
     15 ohms to 44 megohms and the temperature coefficients of resistance
     at 25°C. from -1.0 to 5.5%/°C. The material used is magnesium ortho-
     titanate (2 MgO).(TiO$_2$) (I). I is an insulator with specific resis-
     tivity of 10^{12} ohm-cm. but is converted to a semiconductor with a
     room temperature specific resistivity of 10^4 ohm cm. by heat treat-
     ment in a reducing atmosphere. Since O is given off the O atoms may
     leave vacancies in the crystal lattice which act as impurity centers
     or reduction may take place on the surface with excess metallic atoms
     subsequently diffusing into interstitial positions in the lattice.
     At low temperatures all of the electrons are bound and resistance is
     high; as the temperature increases more electrons break their bonds
     and the resistance decreases. $R = Ae^{\frac{b}{T}}$ where A is a constant contain-
     ing the shape factor; T is temperature in °K., and b is a constant
     proportional to the activation energy. For our thermistor the activa-
     tion energy averages about 0.3 electron volts. Temperature coeffi-
     cient of resistance $\alpha = -\frac{b}{T^2}$. Mg orthotitanate was prepared from MgO
     and TiO$_2$ (50.16% MgO and 49.84% TiO$_2$) mixed by tumbling 30 minutes
     then run through a hammer mill. The powder was pressed into square
     shapes and heated to 1050°C., ground to pass a 120 mesh screen and
     formed into thermistor shapes. Disks were formed by the dry-press
     method, rods by tamping in a brass tube and threads by application
     of a mixture with nitrocellulose to a nylon thread. Each was fired
     at 1000-1200°C. They were then reduced in H at 1350-1450°C. Contacts
     were fixed before or after firing depending on type used.

90. Nechev, G.N.
     TEMPERATURE STABILIZATION OF THERMISTORS.
     Atom i telem. 21 (4), 548-54 (1960).
     (Monthly Index of Russian Accessions 13, 2084 (1960)).

91. New York University.
     INVESTIGATION AND RESEARCH TOWARD DEVELOPMENT OF A SEMI-CONDUCTING
     CERAMIC MATERIAL.
     AD-147,452.
     (Astia Bibliography).

     This study concerns a semiconducting ceramic material with temperature
     coefficient of resistance as near zero as possible from minus 40°C.
     to plus 3.5°C. Materials used are porcelain (flint), steatite (talc)
     and zircon porcelain.

92. Oreshkin, P.T.
ELECTRICAL CONDUCTIVITY OF ALUMINUM AND ZINC OXIDES AT HIGH
TEMPERATURES.
Zhur. Tekh. Fiz. 25, 2447-50 (1955).
(C.A. 50, 5345c).

This investigation was made in view of preparation of thermistor
thermoelements for the measurement of high temperatures. ZnO and
Al_2O_3 were investigated to 1300°. The powders were pressed into
a steel tube, together with a Nichrome wire serving as a second elec-
trode, at a pressure of 5000 atmospheres. The resistance of Al_2O_3
consists of two parts: volume resistance with electronic conductivity
and barrier-layer resistance with hole conductivity. Aging increases
the resistance by an increase of barrier-layer resistance. At 1300°
the resistance of Al_2O_3 is of the order of 10^4 ohms. ZnO has a low
resistance above 1000°, and it is thus unsuitable for thermistors at
high temperatures.

93. Oreshkin, P.T.
HIGH-TEMPERATURE THERMISTORS (SEMICONDUCTOR RESISTANCE THERMOMETERS).
Izvest. Akad. Nauk SSSR., Otdel. Tekh. Nauk 1956 (8), 128-30.
(C.A. 51, 3201b).

Pressed rods of Al_2O_3, MgO, ZnO, and MgO + Al_2O_3 were tested for use
as high-temperature pyrometers at temperatures up to 1570°. The
results obtained with Al_2O_3 were readily reproducible with a scatter-
ing of ± 10° for the different samples, but the values obtained with
MgO were not dependable.

94. Oreshkin, P.T.
EXPERIMENTAL MODELS OF A HIGH TEMPERATURE THERMISTOR.
Zhur. Tekh. Fiz. 28, 1408-12 (1958).
(Physics Abstracts 62, No. 3403 (1959)).

The semiconductor resistance thermometer (S.R.T.) consisted of Al_2O_3
elements between SiC electrodes. It was shown that although the con-
ductivity of the measuring elements decreased (sometimes by a factor
of 10) during the first 50 hours at 1500°...the stability after this
preliminary annealing was quite satisfactory..It is concluded that
SRT's of this type are suitable for temperature measurements at 1000-
1600°C.

95. Padmos, Adriaan, and Evert J.W. Verwey (to Hartford National Bank and
Trust Co.).
RESISTANCE ELEMENTS.
U.S. 2,468,450, Apr. 26, 1949.
(C.A. 43, 5682f).

Resistance elements are prepared by sintering a mixture of Mg and Ti
oxides at 1700-2000° in a gas stream containing H and O, the O con-
centration being in excess of 0.003% of the H concentration...

96. Patent-Treuhand-Gesellschaft für elektrische Glühlampen m.b.H.
    ELECTRIC RESISTANCES HAVING A NEGATIVE TEMPERATURE COEFFICIENT.
    Ger. 712,538, Sept. 25, 1941.
    (C.A. 37, 4310[4]).

    The resistances are made of a mixture of nonconducting oxides and
    conducting lower oxides. At the most 75% of the mix is TiO_2 and
    (or) Cb_2O_3 and (or) V_2O_5. The nature of these oxides is such that
    they do not reduce to metal at 800-1500° in an atmosphere of H.
    The rest of the mix is made up of an alkaline earth oxide, especially
    MgO. The alkaline earth oxide should not decompose during the pre-
    paration nor in operating the resistance and should have a specific
    resistance 10^5 ohms per cm. The mix is shaped and fired first in an
    atmosphere containing O and then in a neutral or reducing atmosphere.
    The firing is such that the Ti, Cb and (or) V oxides are reduced to
    lower oxides having a specific resistance of 10 ohms per cm.

*97. Paterson, W.L.
    CHARTS GIVE THERMAL CHANGES OF THERMISTORS.
    Electronics 32, 128, Oct. 23, 1959.
    (App. Sci. and Techn. Index 1960, 434).

    A chart showing the relation of resistance to temperature for therm-
    istors, based on the equation $X = Ae^{\frac{B}{T}}$ where X is resistance, A is a
    constant having the same dimensions as X; B is a constant depending
    on activation energy and T is absolute temperature.

98. Pearson, G.L., and J. Bardeen (Bell Telephone Labs, Inc.).
    ELECTRICAL PROPERTIES OF PURE SILICON AND SILICON ALLOYS CONTAINING
    BORON AND PHOSPHORUS.
    Physical Reviews 75, 865-883 (1949).
    (Physics Abstracts 52, No. 6199 (1949)).

    Measurements of electrical resistivity and Hall effect over a
    temperature range from 0.0005 to 1% β (p-type impurity) or ρ
    (n-type impurity) were used. X-ray measurement showed that the
    impurity centers occupy lattice positions. The width of the forbidden
    band was found to be 1.12 e.v. The activation energy associated with
    acceptor impurity levels is 0.08 e.v. for very low impurity contents,
    increases with increasing impurity content and vanishes for concen-
    trations above 5×10^{18} centers per cm.[3]. Activation energies associ-
    ated with donor levels are generally smaller than those of acceptor
    levels...

99. Pereleshina, A.P. (Krzhizhanovskii Inst. of Power Engineering, Moscow).
    RESULTS OF AN EXPERIMENTAL INVESTIGATION OF THERMOELECTROMOTIVE FORCE
    IN THERMISTORS.
    Inzhener.-Fiz. Zhur., Akad. Nauk Belorus SSR No. 4, 119-22 (1960).
    (Nuclear Science Abstracts 14, No. 20723 (1960)).

    Results are given of an experimental investigation of the thermal and
    electrical properties of disc thermistors made from AgCl, CuO, Ag_2S,
    Mn_2O_3 and MnO. Results lead to the conclusion that it is possible to
    use these thermistors for the measurement of heat flow...

100. Pereleshina, A.P.
      PHYSICOCHEMICAL PROPERTIES OF THERMISTORS MADE OF MANGANESE DIOXIDE.
      Akad. Nauk SSSR. Energeticheskiz inst. imeni G.M. Krzhizhanovskogo.
      Problemy energetiki, Moskna 1959, 828-48.
      AD-257,908.
      (Astia Bibliography).

      The results of experimental investigations of the electrical and
      thermal properties of thermistors made of Mn oxides show them to
      be solid electrolytes. Theoretical formulas are derived for
      temperature dependence of coefficient of heat conductivity
      and thermal e.m.f. and dependence of resistance on temperature and
      of charge mobility on activation energy are empirically characterized.
      In thermistors of Mn oxides, oxygen ions are the charge carriers.
      In the presence of a temperature gradient in a thermistor semiconduct-
      ing substance a non-uniform concentration of O ions appears which
      leads to the appearance of an e.m.f. in the thermistor.

101. Perrone, Guy
      PROPERTIES AND APPLICATIONS OF THERMISTORS.
      Chaleur et Ind. 36, No. 354, 3-13 (1955).
      (C.A. 49, 4909c).

      A review with 20 references.

102. Peters, Melville F. (to Petcar Research Corp.).
      THERMISTOR FOR HIGH-TEMPERATURE MONITORS.
      U.S. 2,596,284, May 13, 1952.
      (C.A. 46, 7914e).

      The skeleton of the thermistor is made by sintering a mixture of
      steatite and flour at 1800°F. (cf. U.S. 2,495,867, C.A. 44, 2724g).
      This skeleton is impregnated with a temperature-sensitive material,
      such as e.g. I sulfide dissolved in alcohol, after which it is
      dried at 200-300°F. Other soluble metal compounds which may be
      used to impregnate the skeleton are Mn, Fe, or Ni acetates, $FeCl_2$,
      $ZnCl_2$, Fe sulfate, $Na_2Cr_2O_7$, or any other soluble metallic compound
      which upon heating changes into an insoluble oxide. The tempera-
      ture responsiveness of the thermistor will depend upon the used
      impregnating material, the concentration of the solution, and the
      number of impregnations. Increasing the concentration of the im-
      pregnating solution lowers the resistance of the thermistor and
      causes it to become conductive at a lower temperature.

*103. Petrov, I.N.
      THERMISTORS.
      Poluprovodnikovyye Pribory (Semiconductor Devices) Moscow, 1957.
      Chapter 2 Section 5.   LC or SLA mi.-$2.40 pH 3.30, No. 60-13532.
      (Translation).
      (OTS Selective Bibliography - Semiconductors SB-429).

      Information is reviewed on properties, types, and practical uses
      of thermistors.

104. Philips' Gloeilampenfabrieken.
     SINTERED ELECTRIC RESISTANCE CONSISTING OF A SPINEL.
     Dutch 73,130, Sept. 15, 1953.
     (C.A. 48, 8094d).

     A sintered electrical resistance having a high negative temperature
     coefficient consists of mixed crystals of Fe_3O_4 and a spinel $2RO.-$
     $R'O_2$, in which R is a bivalent element and R' a quadrivalent ele-
     ment, such as Mg_2TiO_4, Zn_2TiO_4, Ni_2TiO_4, and Zn_2SnO_4, or their
     mixed crystals, less than half the molecules being Fe_3O_4. To obtain
     a resistance having a low negative temperature coefficient, more
     than half the molecules should be Fe_3O_4, in which case a second
     phase, consisting of an insulating bivalent oxide can be present
     to raise the specific resistance and regulate the temperature co-
     efficient, which oxide dissolves badly in the spinel mass and is
     distributed evenly therein, such as MgO and ZrO_2. If the spinel
     phase is not supersaturated with a second phase at about 500°,
     separation of a second phase above 500°, effecting undesired changes
     of the resistance properties, is impossible. At lower temperature
     the velocity of separation is so low that no trouble can be caused.
     In an example 0.376 mole Fe_2O_3, 1.5 mole NiO, and 0.75 mole TiO_2
     are ground with alcohol in a ball mill for 16 hours. The dried
     mass is worked with a 20% solution of the Me methacrylate in methyl
     glycol acetate to a moldable mass and pressed in a stuffing press
     into bars of 4 mm. diameter, which are sintered at 1300° for 1 hour
     in an atmosphere of pure N (O content about 0.1%) and then are
     rapidly cooled in a N current. At 22° the specific resistance is
     22,000 ohms cm., at 138° 900 ohms cm., at 227° 200 ohms cm., and
     at 332° 50 ohms cm.

105. Philips' Gloeilampenfabricken.
     ELECTRICAL RESISTANCES.
     Brit. 468,477, July 6, 1937.
     (C.A. 32, 57⁶).

     A resistance having a negative temperature coefficient and formed
     from a sintered semiconductive mixture containing ceramic material
     and a preponderating amount of Si or Si alloy is simultaneously
     provided with end contacts by assembling together the resistance
     material and carbonaceous contact masses, the whole unit being
     heated to a temperature sufficient to sinter the mixture but not
     fuse the Si or Si alloy and cause the mixture and the contact masses
     to adhere. In an example, Fe-Si, clay and tragacanth are powdered
     and mixed into a paste with H_2O and pressed into rods and small
     graphite blocks are pressed into the ends; the rods are dried and
     sintered at 1300° in a reducing gas atmosphere. Small rods of Ni
     may serve as leads.

106. Polye, William R. (Bendix Aviation Corp.).
     HEATED THERMISTOR.
     U.S. 2,878,351, Mar. 17, 1959.
     (Ceramic Abstracts 1959, 187g).

     A heated thermistor comprises a rod-shaped ceramic thermistor, a
     layer of ceramic insulation surrounding the thermistor, and a layer
     of graphite surrounding the insulation layer.

107. Prigent, J.
      INVESTIGATION OF URANIUM OXIDE THERMISTOR.
      J. Phys. Radium 10, 58-64 (1949).
      (Physics Abstracts 52, No. 2513 (1949); C.A. 43, 7346h).

      Amorphous UO_2 is preferred, as it makes better contact than the
      crystalline form; details of preparation for uranyl nitrate are
      given. Resistance varies with pressure according to $1/R = cP^{\&}C$,
      c and C being constants for a given thermistor. Resistance in
      opposite directions vary by about 1 to 500. Resistance decreases
      with time at first, taking 30 minutes to reach a constant value
      5% less than the original value. Resistance at 50 volts is approxi-
      mately 1/2 that at 1 volt. Resistance at 100°C. is approximately
      1/4 that at 50°. Thermistors may be used as resistance thermometers
      reading to 1/160°C., or as sensitive infrared bolometers. Their
      high resistance makes them unsuitable for cm. and wave detectors.

*108. Rodgers, G.B., and F.A. Raal (Diamond Research Lab., Johannesburg,
       South Africa).
       SEMICONDUCTING DIAMONDS AS THERMISTORS.
       Rev. Sci. Instr. 31, 663-4 (1960).

109. Sachse, Herbert B. (Keystone Carbon Co., St. Marys, Pa.).
      LOW-RESISTANCE THERMISTORS AS ULTRA-COLD THERMOMETERS.
      Electronic Inds. Tele-Tech 16 (1), 55, 142-3, 146-7 (1957).
      (C.A. 52, 1695h).

      At liquid-O temperatures new thermistors exhibit resistance
      characteristics as low as 300 ohm-cm. and temperature coefficients
      as high as 35% per degree.

110. Sanborn, Paul H.
      FERRIC OXIDE-TITANIUM DIOXIDE MIXTURES AS ELECTRICAL CONDUCTORS.
      U.S. 2,590,894, Apr. 1, 1952.
      (C.A. 46, 5288a).

      Fe_2O_3-TiO_2 with clay is formed into a ceramic body, leaving a
      negative temperature coefficient of resistance, by the usual methods.
      The articles are useful in the measurement of temperatures, tempera-
      ture control of relays, for voltage regulation, as thermoresponsive
      resistors for motor starting, as lightning arrestors, etc.

*111. Sapoff, Meyer.
       THE THERMISTOR - A SPECIALIZED SEMICONDUCTOR SENSOR.
       Military Systems Design 5 (4), 14-19 (1961).

       Although the structure and mechanism of conduction in monocrystalline
       semiconductors is fairly well understood, their use as thermistors
       has been very limited to date. At present almost all commercial
       thermistors are fabricated from oxide semiconductors. Unfortunately
       no quantitative theory exists which adequately explains the behavior
       of oxide semiconductors. Some qualitative insight may be obtained
       by comparing their properties with those of single-crystal doped
       elements...Oxides of NiO and Cu_2O are called "p" type semiconductors,
       of ZnO and TiO_2, "n" type.

112. Sauer, H.A., and J.R. Fisher.
      PROCESSING OF POSITIVE TEMPERATURE COEFFICIENT THERMISTORS.
      J. Am. Ceramic Soc. 43, 297-301 (1960).
      (Ceramic Abstracts 1960, 163d).

      The controlled addition of impurities such as La in ceramic Ba
      titanate and BaSi titanate semiconductor systems results in therm-
      istor materials having large positive temperature coefficient of
      resistance over controled temperature ranges (9-6-12.5% per °C.
      at 25-50°C.). The resistivity in these systems is sensitive to
      the concentration of the trace additives, to undesirable impurities
      in the raw materials and to the sintering and maturing conditions.
      Ceramic procedures well adapted to prepare these thermistors repro-
      ducibly have been developed.

113. Scarr, R.W.A., and R.A. Setterington.
      THERMISTORS, THEIR THEORY, MANUFACTURE AND APPLICATION.
      Inst. E.E. Proc. 107 Part B, 395-409, Sept., 1960.
      (App. Sci. and Techn. Index 1960, 434).

*114. Schiff, R.I.
      THERMISTORS.
      Instruments and Control Systems 33, 83 (Jan. 1960).
      (App. Sci. and Techn. Index 1960, 434).

115. Schottky, Walter (to Siemens and Halske A.-G.).
      THERMONEGATIVE RESISTORS.
      U.S. 2,183,755, Dec. 19.
      (C.A. 34, 2264⁹).

      A resistor with a descending characteristic may comprise a wire-
      or ribbon-like α-conductor of material such as CuO or UO₂ embedded
      in a refractory insulating material.

116. Science and Tech. Section, Air Information Div., Washington, D.C.
      MANGANESE OXIDE THERMISTORS. Special Translation from "Physico
      Chemical Properties of Thermistors Made of Manganese Oxides";
      Akad. Nauk SSSR. Energeticheskiy Inst. Imeni G.M. Krzhizhanovskogo.
      Problemy Energetiki. Moskva, p. 828-48 (1959).
      AD-257,908, June 22, 1961 (OTS 3.60).
      (TAB 61-3-4, p. 23 (1969)).

      Experimental investigation of the electrical and thermal properties
      of thermistors made on manganese oxides confirms the correctness of
      the hypothesis which states that the investigated specimens are
      actually solid electrolytes. Theoretical formulas are derived for
      the temperature dependence of the coefficient of heat conductivity
      and thermal e.m.f. Empirical laws are determined to characterize
      the dependence of the resistance of specimens on temperature, and
      the dependence of the charge-carrier mobility in the specimens on
      activation energy. In thermistors made of manganese oxides, O ions,
      which are the charge carriers, also take an active part in the pro-
      cess of heat transport. In the presence of a temperature gradient
      in a thermistor semiconducting substance, a nonuniform concentration

of O ions appears which leads to the appearance of an e.m.f. in the thermistor.

117. Schwartzwalder, Karl, Alexander S. Rulka, and Robert W. Smith (to General Motors Corp.).
RESISTOR FOR TEMPERATURE INDICATORS.
U.S. 2,480,116, Aug. 30, 1949.
(C.A. 43, 9407i).

A ceramic resistor having a large and uniform temperature coefficient of electrical resistance and other desirable properties is composed of magnetite 71.1, Fe_2O_3 8.9, borosilicate glass (Pyrex) 10 and Mg borate glass 10%. It is chemically stable and unaffected by oil or grease, but slightly soluble in H_2O and must be protected from it. Elimination of Mg borate glass from the recipe improves stability to H_2O.

118. Shashkov, A.G.
POLARIZED THERMISTOR.
Trudy Inst. energ. ANBSSR 6, 216-21 (1958).
(Monthly Index of Russian Accessions 13, 680 (1960)).

119. Sheftel, I.T.
SEMICONDUCTORS AS THERMALLY SENSITIVE RESISTORS (THERMISTORS).
Poluprovod. v Nauke i Tekh., Akad. Nauk S.S.S.R., Inst. Poluprovod. 1, 249-90 (1957).
(C.A. 54, 61h).

120. Silver, Roland (Electronics Corp. of America).
RESEARCH IN THERMAL-RESISTANCE EFFECTS.
AD-130,844, June 1957.
(Astia Bibliography).

A study has been made to investigate the properties of film-type thermistors and their application to computer circuitry. An extensive bibliography, and a discussion of theory derived from these references, are presented together with basic circuitry for various applications. A few thermistors of the thin-film semiconductor type were constructed, including an array of ten elements. Tests made on these experimental units corroborated the theoretical data and computations, and established the feasibility of using thermistors as medium-speed switching units of very small size and little weight in computer circuitry. Further studies of many more potential thermistor materials, and of practical applications of them are recommended.

121. Skaupy, F. (Berlin-Lichterfelde, Germany).
THE HISTORICAL DEVELOPMENT OF THE SEMICONDUCTOR PROBLEM AND OF SEMICONDUCTOR RESISTORS.
Z. Elektrochem. 54, 1959-60 (1950).
(C.A. 44, 9832f).

Historical data on the development of semiconductors in Germany. Skaupy proposed as early as 1920 the use of ZnO as resistor with negative temperature coefficient.

122. Smith, H.A.
      TEMPERATURE MEASUREMENT BY THERMISTORS AS APPLICABLE TO TELEMETRY.
      AD-123,600, Dec. 1956.
      (Astia Bibliography).

      This memo describes the theory, and practical application, of
      thermistors used in potential dividing devices to give voltage
      outputs related to temperature. These, unamplified, can be tele-
      metered, and recorded by ground or remote equipment.

123. Smith, Otto J.M. (University of California, Berkeley).
      THERMISTORS. PART I. STATIC CHARACTERISTICS.
      Rev. Sci. Instr. 21, 344-50 (1950).

      The fundamental thermistor equations are presented as functions
      only of electrical quantities and constants, and independent of
      temperature measurements. The universal curves allow one to
      predict the static characteristics of thermistors as circuit
      elements. The two most significant characteristics are the power
      coefficient of resistance and the negative incremental resistance.
      These can be computed or read from the universal curves, if the
      resistance and 4 parametric constants are known. These 5 values
      can be determined from 6 convenient measurements: the resistance
      and change of resistance with current at very low current, at the
      maximum voltage point, and at maximum current.

124. Smith, Otto J.M.
      THERMISTORS. DYNAMIC CHARACTERISTICS. PART II.
      Rev. Sci. Instr. 21, 351-6 (1950).

      A thermistor is a resistance with a high negative temperature
      coefficient of resistance. They are semiconductors similar to
      Thyrite except that their resistance changes with temperature
      instead of applied voltage. They are usually made of fused oxides
      of Ni, Mn and Co, and are extremely stable for long lengths of time.
      They can be used for sensitive temperature inducting devices
      because the resistance change is about 4% per °C. They can be
      used as sensitive bolometers for microwaves or visible light if
      connected in a bridge current to balance out ambient temperature
      changes. A thermistor can be used as a non-linear circuit
      element in many of the same applications as a C-filament light
      bulb. They can be used as voltage regulators, amplitude stabilizers,
      volume expanders and volume control devices. The thermistor sinus-
      oidal and transient response characteristics are presented as a
      function of the dissipation constant and incremental resistance.
      Equations are given for time constant, critical frequency, equiva-
      lent inductance, and Q. The construction of a low frequency
      oscillator is discussed, as well as possible non-linear filter
      applications.

125. Smith, R.A.
      THERMISTORS, VARISTORS AND OTHER NON-LINEAR RESISTORS.
      Semiconductors. Cambridge, England, The University Press (1959),
      p. 479-481.

      The thermistor consists of a small bead of semiconducting material
      used as a bolometer. In commercial units a mixture of semiconduc-
      tors chosen to give a high temperature coefficient of resistance
      but not too high a resistance is used. The bolometer element
      generally consists of a mixture of the oxides of Ni, Mn and Co.
      Non-ohmic resistors from granulated SiC are widely used. These
      are commonly called "varistors".

* 126. Smith, R.W. (AC Spark Plug Division, General Motors Corp.).
      THERMISTORS - THE STORY OF THERMALLY SENSITIVE SEMICONDUCTORS.
      Ceramic Ind. 74 (5), 79-81; (6), 84-7; 75 (8), 74-7 (1960).
      (App. Sci. and Techn. Index 1960).

  127. Smith, Robert W., and Karl Schwartzwalder (to General Motors Corp.).
      AN ELECTRIC RESISTOR WITH A NEGATIVE TEMPERATURE COEFFICIENT.
      U.S. 2,786,819, March 26, 1957.
      (C.A. 51, 7909d).

      A resistor was prepared which can be used as a thermistor having
      a negative temperature coefficient. Partially oxidized metal
      oxides, such as NiO, Ni_2O_3, Fe_2O_3, $FeO \cdot Fe_2O_3$, Co_3O_4 and Ti_2O_3 in
      various ratios, were used, with a glazing substance to exclude O
      from the individual particles. Such a thermistor composed of Mg
      borate glass 15, No. 774 Pyrex 25, Sierra talc 22, and $FeO \cdot Fe_2O_3$
      38%, when cycled between room temperature and 1100°F. for 48 hours
      at 40 cycles per hour, underwent a 12% decrease in resistance.

  128. Société Prosilis.
      SEMICONDUCTORS.
      Fr. 991,891, Oct. 11, 1951.
      (C.A. 50, 9164a).

      Semiconductors, the electrical resistance of which varies strongly
      with temperature, consist of solid solutions of a conducting oxide,
      e.g., V, Ti, Pr oxide, in a preferably isomorphic isolating oxide,
      e.g., Al_2O_3, ThO_2, Cr_2O_3, and are made by pressing and sintering
      a powdered mixture of the oxides. Thus powdered TiO_2 and V_2O_5
      (200 mesh) are mixed in the desired proportions, the mixture is
      shaped by pressure of 5 tons/sq. cm., dried by heating to 200°,
      and sintered at 1100-1250°.

  129. Standard Telephone and Cables, Ltd.
      ELECTRIC RESISTANCES.
      Brit. 492,431, Sept. 20, 1938.
      (C.A. 33, 1604⁴).

      A resistor having a high negative temperature coefficient comprises
      a granule consisting of a crystal of B or a cluster of B crystals,
      permanently joined to lead wires, e.g., of Pt, Pd, or Fe, by a
      compound of B and the metal lead wire...

130. Standard Telephone and Cables, Ltd.;, Henry Wolfson and Leonard
      J. Harris.
      RESISTANCES.
      Brit. 501,528, Feb. 28, 1939.
      (C.A. 33, 5756[7]).

      A resistance element consisting of a metallic compound having a
      negative temperature coefficient is provided with metal contacts
      that are secured initially to the metal body, which is subsequently
      treated to form the compound, the contacts being formed of a metal
      or alloy unaffected by the treatment. Thus, Ag_2S resistances are
      produced by binding contact wires of W or a Ni-Cr alloy, e.g.,
      "Brightray," "Nichrome," tightly around grooves in a Ag rod, the
      assembly being then exposed to S vapor at 300-400° for 15 minutes
      or longer to convert the Ag to Ag_2S after which the element is
      stabilized by being heated to 200-300° in N or other inert gas.

131. Standard Telephones and Cables, Ltd., and Ernest F. Dearborn.
      RESISTANCE MATERIALS.
      Brit. 540,844, Oct. 21, 1941.
      (C.A. 36, 4638[3]).

      A material of negative temperature coefficient of resistance com-
      prises the combined oxides of Ni, Mn and Co. The specific resis-
      tance of the material depends upon the relative proportions of Ni,
      Mn and Co in the combination.

132. Suchet, Jacques, and N'Guyen Thien-Chi.
      NEGATIVE-TEMPERATURE-COEFFICIENT RESISTANCES AND COATINGS FOR THEM.
      U.S. 2,720,471, Oct. 11, 1955.
      (C.A. 50, 2896a).

      Thermistors having resistances of the order of 100 ohms/cm. at
      300-1000° are described. They consist of a fritted, homogeneous
      mass of finely divided metallic oxides of Ti, V, Cr, Mn, Fe, Co,
      Ni, or Cu, along with ≥ 10% by weight of a refractory oxide, e.g.,
      Al_2O_3 and (or) SiO_2. Preferably, the metallic oxide mixture con-
      sists partly of Mn_2O_3. These mixtures should also contain Mn
      40-80, Ni 3-14, Co 10-17 and Fe 1-10%. If Cu oxides are present,
      the amount of Cu should be 8-30%. The thermistors must be coated
      with a refractory, gas-tight, chemically resistant material, e.g.,
      a silicate or borosilicate of Pb or Zn. For example, 67% Mn_2O_3
      and 16% NiO were mixed with 18% Al_2O_3 in a jar made of nonoxidiz-
      able alloy having great hardness. Balls of tungsten carbide were
      put into the mixture and the jar was partially filled with liquid.
      After tightly closing the jar, it was rotated for about 400 hours.
      The powder obtained was molded under very high pressure into small
      rods and then fired in a special furnace. Connections were then
      fixed to the rods which were then stabilized. The material had a
      resistivity of 100 ohms/cm. and a temperature coefficient of 0.014
      ohms/ohm/°C. at 430°. For use at high temperatures, a mixture of
      PbO 55, ZnO 20, Al_2O_3 10, SiO_2 5, and B_2O_3 10% was ball-milled for
      50 hours, made into a paste with water, applied as a coating, and
      fired at 650°.

133. Tavernier, P., and P. Prache.
      INFLUENCE OF PRESSURE ON THE RESISTIVITY OF A THERMISTOR.
      J. Phys. Radium 13, 423-6 (1952).
      (Physics Abstracts 56, No. 812 (1953)).

      The variation in resistance, expressed as the fractional change
      $\Delta R/Ro$ of a thermistor kept at a constant temperature and sub-
      jected to various pressures P up to 5000 kg. cm.$^{-2}$, is represented
      by the equation $\Delta R/Ro = 4.6 \times 10^{-6}$ P. This relation holds almost
      exactly for any given temperature in the range 30-70°C. The
      thermistor-controlled thermostatic bath used in the experiments
      is described.

134. TEMPERATURE MEASUREMENTS AT ABSOLUTE ZERO.
      Electronics 31, 84 (Apr. 25, 1958).
      (Semiconductor Electronics 2, No. 1925).

      A Ge resistance thermometer with high sensitivity and stability
      in the absolute zero temperature range has been developed by J.E.
      Kunzler, T.H. Geballe, and G.W. Hull of Bell Telephone Labs...
      A very small "bridge" cut from a single crystal of As-doped Ge is
      the basic element...Ge can be doped with As to produce a high and
      fairly constant temperature coefficient of resistance of about 1
      ohm at room temperature, 14 ohms at 10°K. and 216 ohms at 2°K.
      Both the temperature coefficient and the actual resistance vary
      widely with minute changes in the amount of doping. This makes it
      possible to fabricate a thermometer having any of a wide range of
      characteristics...

135. THERMISTOR DATA CHART.
      Electronic Design 6, 20-25, Apr. 30, 1958.
      (Semiconductor Electronics 2, No. 2634 (1958)).

      A tabulation of thermistors produced by several manufacturers
      is presented. The characteristics (cold resistance, dissipation
      constant, time constant, and temperature coefficient) listed in
      the table are described.

136. Tyler, W.W., and H.H. Woodbury.
      PROPERTIES OF GERMANIUM DOPED WITH IRON. I. ELECTRICAL CONDUCTIVITY.
      Physical Reviews 96, 874-82 (1954).

      Measurements of the temperature dependence of electrical resistivity
      in p- and n-type iron-doped Ge crystals indicate that Fe introduces
      impurity levels in Ge at 0.34 $\pm$0.02 e.v. from the conduction band.
      Such samples show very high resistivity at 77°K...

137. Tyler, W.W., R. Newman, and H.H. Woodbury (General Electric Research
      Lab, Schenectady).
      PROPERTIES OF GERMANIUM DOPED WITH COBALT.
      Physical Reviews 97, 669-72 (1955).

      Measurements of temperature dependence of electrical resistivity
      in n- and p-type cobalt-doped Ge crystals indicate that Co intro-
      duces acceptor levels in Ge at 0.31 ± 0.01 e.v. from the conduc-
      tion band and 0.25 ± 0.01 e.v. from the valence band...

138. Tyler, W.W., and R. Newman (to General Electric Co.).
      BISTABLE SEMICONDUCTOR DEVICES.
      U.S. 2,871,377, Jan. 27, 1959.
      (Semiconductor Electronics 3, No. 3535 (1959)).

      Semiconductor devices which utilize the process of injection
      breakdown to provide 2 alternative values of resistance within
      a given range of operating values are described. The semiconductor
      crystal is doped with Fe, Co, Au, Zn or Cu to provide deep-lying
      energy levels within the forbidden band. Injection breakdown in
      the semiconductor is believed due to the cumulative effect of
      minority carriers which are injected at a junction. At liquid
      air or liquid nitrogen temperatures the resistance of these devices
      can be made to change by a factor of 10^9 to 10^{10} by a pulse of
      voltage or light sufficient to initiate the breakdown. Both 2-
      terminal and 3-terminal devices are described...These devices are
      suitable for switches, relays, voltage regulators, over-voltage
      detectors, light detectors and temperature sensors.

139. Tyler, W.W., and R. Newman (to General Electric Co.).
      GERMANIUM CURRENT CONTROLLING DEVICES.
      U.S. 2,871,427, Jan. 27, 1959.
      (Semiconductor Electronics 3, No. 3686 (1959)).

      A thermosensitive device and a photo-conductive cell which are
      highly sensitive in the temperature range from 0 to -200°C. and
      a high-voltage rectifier which can operate at frequencies up to
      1/2 megacycle are described. All of these devices utilize Ge
      doped with a trace of Fe, which introduces deep-lying trapping
      levels and thereby radically alters the resistivity vs. tempera-
      ture curve of the germanium...

140. Udalov, N.P.
      MORE ON THE CALUCLATION OF THERMISTOR CHARACTERISTICS.
      Autom i telem. 20 (6), 825-7 (1959).
      (Monthly Index of Russian Accessions 13, 316 (1960)).

141. Udalov, N.P.
      SEMICONDUCTOR THERMAL RESISTORS.
      Inzh.-fiz. zhur. No. 1, 126-7 (1960).
      (Monthly Index of Russian Accessions 13, 1465 (1960)).

      Review (by L. Voloshin) of book of this title.

*142. Ullman, Eleanor M. (Thermistor Corp. of America).
       HOW TO USE THERMISTORS.
       Electronic Equipment 1956, June.

       A brief history of thermistors and recent developments in their
       manufacture, as well as design information, are given.

143. . University of Denver, Colorado (D.E. Rugg).
       TEXACO THERMISTOR TESTS AND RESULTS.
       AD-252,009, Jan. 1961.
       (Astia Bibliography).

       Six boron thermistors, 3 bead type and 3 cylindrical, were
       produced and evaluated. At 25° their properties are as follows:

Temperature	TPJ-3 25°	TPJ-4 25°	TPJ-5 25°	TRR-2	Vecco 51A22
Voltage	9.32 v.	9.32 v.	9.32 v.	1.58 v.	0.40 v.
Current	066 μa	075 μa	062 μa	.615 μa	3.10 μa
Resistance	141 meg	124 meg	150 meg	2.5 meg	1.29 K
$\frac{\Delta i}{\Delta T}$	0037 $\frac{\mu a}{°C}$	0052 $\frac{\mu a}{°C}$	0033 $\frac{\mu a}{°C}$	033 $\frac{\mu a}{°C}$	.134 $\frac{\mu a}{°C}$
α	5.6%/°C	6.9%/°C	5.3%/°C	5.4%/°C	43%/°C
β	5000° K.	6100° K.	4700° K.	4800° K.	3800° K.

144. Vander Beck, Roland R., Jr. (Carborundum Co.).
       SILICON CARBIDE RESISTANCE BODIES AND METHODS OF MAKING.
       U.S. 2,916,460, Dec. 8, 1959.
       (Ceramic Abstracts 1960, 90b).

       A method of making recrystallized silicon carbide thermistor
       bodies comprises forming a body from a mixture of SiC particles
       and a small amount of a boron compound to provide 0.20 to 0.34%
       (weight) boron in the lattice of the SiC when recrystallized and
       firing the shape at 2000° to 2500° C. to recrystallize the SiC
       and introduce the boron into the SiC crystal structure.

145. Van Dover, James, and Norman F. Bechtold (U.S. Army Signal Research
       and Development Lab., Fort Monmouth, N.J.).
       SURVEY OF THERMISTOR CHARACTERISTICS.
       Electronics 33 (7), 58-9 (1960).

       Industry is finding more and more use for thermistors...To make
       electronic circuits reliable, thermistors compensate for tempera-
       ture changes, regulate current or voltage and control remote cir-
       cuits. In the medical, meteorological and mechanical fields,
       thermistors are used for accurate measurement of temperature,
       pressure and liquid levels.

TABLE I NEGATIVE-TEMPERATURE-COEFFICIENT THERMISTORS

Type	Resistance Range at 25°C. ohms	Max. Rating watts	Dissipat'n Constant at 25°C. mw/°C.	Max. Operat. Temp. °C.	Temp. Coef. %/°C.	Time Const. sec.	Dimensions inches	Primary Applications
Glass-coated Bead	100-12 M(a)	0.2	0.09-0.8	500(e)	-3.1 to -5.2	0.5-3	0.006-0.110 diam	wind velocity, temp. gas analysis, liquid level, power control.
Bead in Container(b)	100-5.3M(a)	0.2	1	500	-3.1 to -5.1	1-25	0.1 diam 1/2-3 long	time delay, medical probe, voltage control, very low temperature.
Disc	4 to 10K(d)	4	3-800	150(e)	-3.8 to -4.4	2-200	0.1-1.1 diam	temp. comp., fire alarms, osc. ampl. stabilization, temperature control.
Rod	2K-100K(d)	2	2.5-6	150(e)	-3.8 to -4.4	20-95	1/4-2 long	filament protection, voltage control and reg. meterological temp. measurement.
Washer	10-1,100	10	100-850	150	-3.8 to -4.4	4-24	1/2-4 diam	higher-power temp. comp., surge suppression.
Wafer	10-1 M(a)	0.5	2.5-7.8	150	-3.9 to -6.8	7-35	1/16 to 1/2 square	temperature measurement and control, high-temperature alarm.

(a) $M = 10^6$; (b) Container is glass probe or bulb; (c) Special units go to 1,200C; (d) $K = 10^3$; (e) 125 C with soldered leads.

TABLE II POSITIVE-TEMPERATURE-COEFFICIENT THERMISTORS

Type	Resistance Range at 25° C. ohms	Max. Rating watts	Max. Operat. Temp. °C.	Temp. Coef. %/°C.	Time Constant sec.	Dimensions inches	Primary Applications
Rod	100-1,000	1/4	100	+0.7	35-54	0.4-0.6 long	Transistor temperature comp. temperature measurement.
Sealed(a) metal case	100-1,000	1/8	125	+0.7	54	0.350 diam 0.245 long	Transistor temperature comp. in high-humidity ambients.
Glass probe	100-1,000		200	+0.7	9	0.078 diam 0.5 long	Temperature measurement and control.

(a) Hermetically sealed.

146. Vepřek, J.
MAIN PRINCIPLES OF THE DESIGN OF THERMISTOR THERMOMETERS.
Staboproudy Obzor (Czechoslavakia), Vol. 21, No. 12, 697-704 (1960)
in Czech.
(Physics Abstracts 64, No. 4503 (1961)).

The principal characteristics of bead-type thermistors are discussed;
in particular, the dependence of their resistance on temperature and
current is analysed. It is pointed out that a bead thermistor can
be used as a temperature transducer and, by connecting it in a resis-
tance-bridge circuit, a thermistor thermometer can be designed. The
operating conditions of the thermistor in the bridge are considered,
and design formulae for the following cases are derived: (1) multi-
purpose thermometer with a direct-reading meter (the diagonal resis-
tance is much lower than the resistances of the bridge arms), (2)
single-purpose thermometer with direct indication, (3) multi-purpose
thermometer with an indirect-indicating instrument (the diagonal
resistance is much higher than the resistance of the bridge arms),
and (4) single-purpose thermometer with indirect indication. It is
shown that the thermometers are stable and accurate, if the thermistor
operating current is suitably chosen. Two practical thermometers for
temperatures of 35-42°C. and 30-60°C. are described.

147. Verwey, Evert J.W., Pieter W. Haayman, and Arie Bol (to Hartford
National Bank and Trust Co.).
ELECTRIC RESISTANCE ELEMENT.
U.S. 2,475,864, July 12, 1949.
(C.A. 43, 8920a).

A resistance element with a negative coefficient of resistance is
prepared by sintering FeO, Fe_2O_3, MgO and CrO_3 in the molecular
ratio of 1:1:2:2, respectively, to form a homogeneous mixed crystal
stable at temperatures above 500°. At temperatures below 500°,
separation into 2 phases takes place, but the separation is very
slow. The $FeO-Fe_2O_3-MgO-CrO_3$ bodies may be sintered at 1400°, while
the corresponding $FeO-Fe_2O_3-MgO-Al_2O_3$ bodies must be sintered at
1500-1600° to obtain a homogeneous and dense product.

148. Verwey, Evert J.W. (to Hartford National Bank and Trust Co., trustee).
ELECTRIC RESISTOR.
U.S. 2,492,543, Dec. 27, 1949.
(C.A. 44, 3691b).

A resistor with negative temperature coefficient is prepared by
sintering at 1400-1500° in an atmosphere of N a mixture of MgO, FeO,
Al_2O_3 and Fe_2O_3 to proportions adjusted to form a spinel phase with
5 to 10 molecular % of MgO and FeO dispersed in the phase.

149.   Verwey, Evert J.W. (to Hartford National Bank and Trust Co.).
        ELECTRIC RESISTANCE.
        U.S. 2,507,233, May 9, 1950.
        (C.A. 44, 6308f).

        An element is prepared which has high electric resistance, with a
        low temperature coefficient which is highly resistant to chemical
        attack, and which can endure high temperature. The element is made
        of MgO with approximately 3% TiO_2 or a lower oxide. Anastase or Me
        cellulose is used as a binder. The rod for the elements is dried
        and sintered at 1700-2000° in an atmosphere of H or H and N, with a
        trace of O.

150.   Verwey, E.J.W., P.W. Haaijman, F.C. Romeijn, and G.W. van Oosterhout
        (Philips Lamp Works, Eindhoven, Netherlands).
        CONTROLLED-VALENCY SEMICONDUCTORS.
        Philips Research Repts. 5, 173-87 (1950).
        (C.A. 44, 10422c).

        A new type of semiconductor is described which contains a fraction
        of ions of deviating valency without the simultaneous formation of
        lattice defects. Such a situation is promoted by incorporation into
        the lattice of foreign ions of such a charge that they balance the
        charge of the ions of deviating valency. X-ray diffraction data and
        electrical conductivity of Li_2O binary systems with CoO and NiO; of
        Fe_2O_3 with TiO_2, alkaline-earth systems with TiO_2 and La_2O_3 are given.
        La_2O_3 greatly reduces the resistance of $SrTiO_3$, $CaTiO_3$, and $BaTiO_3$.
        The following additional systems were studied: Li_2S-MnS, La_2O_3-$CaMnO_3$,
        $SrTiO_3$-$SrZrO_3$-La_2O_3, CaO-$LaMnO_3$, SrO-$LaMnO_3$, SrO-$LaFeO_3$, TiO_2 with
        Ta_2O_5, $ZnFe_2O_4$, $MgFe_2O_4$, $NiFe_2O_4$, $CoFe_2O_4$, Fe_2O_3, and Cr_2O_3-Fe_2O_3,
        SnO_2-Fe_2O_3, WO_3-Fe_2O_3, Sb_2O_5-SnO_2, $MgWO_4$-Cr_2O_3, NiO-MgO-Li_2O, and
        Cr_2O_3-Fe_2O_3-TiO_2. Applications include ceramic resistors with negative
        temperature coefficient.

151.   Verwey, Evert J.W., and Marinus G.v. Bruggen (to Hartford National
        Bank and Trust Co.).
        ELECTRICAL RESISTANCE ELEMENTS WITH NEGATIVE TEMPERATURE COEFFICIENT.
        U.S. 2,524,611, Oct. 3, 1950.
        (C.A. 45, 52g).

        Electrical resistance elements consist of a sintered mass of mixed
        crystals of FeO, Fe_2O_3, MgO, and Al_2O_3 in which the total amount of
        Fe oxides is 50 molecular % or less, and the bivalent and trivalent
        oxides are present in equimolecular amounts. The latter is achieved
        by the proper choice of sintering temperature and atmospheric compo-
        sition.

152. Verwey, Evert J.W. (to Hartford National Bank and Trust Co.).
      ELECTRICAL RESISTORS.
      U.S. 2,616,859, Nov. 4, 1952.
      (C.A. 49, 7923b).

      Fe_2O_3 0.375, NiO 1.5, and TiO_2 0.75 gram-molecules are ball-milled
      16 hours with EtOH, worked with a solution of 20% Me methacrylate
      in Me glycol acetate to form a kneadable mass, extruded as 4-mm.
      rods, sintered 1 hour at 1300° in pure N (containing 0.1% O), and
      cooled rapidly in an N stream to give rods having a specific resis-
      tance of 2200 ohms/cm. at 22°, 900 at 138°, 200 at 227°, and 50 at
      332°. Fe_2O_3 4.5, ZnO 10.2, and TiO_2 5.1 gram-molecules are ground
      with Et acetate for 16 hours, extruded with 10% nitrocellulose in
      ethylene glycol to form tubes 6.3 mm. long, with an external diameter
      of 8 mm. and an internal diameter of 4.5 mm., and heated at 1320°
      as above. The sintering temperatures of combinations of Fe_3O_4 with
      spinel compounds, such as Mg_2TiO_4, Zn_2TiO_4, Ni_2TiO_4, Zn_2SnO_4, or their
      mixed crystals, may thus be reduced to 1300°.

153. Voloshin, I.F.
      THEORY OF SEMICONDUCTING THERMAL RESISTANCES.
      Trudy Inst. energ. ANBSSR No. 6, 193-205 (1958).
      (Monthly Index of Russian Accessions, 13, 680 (1960)).

154. Voloshin, I.F., A.S. Kasperovich, and A.G. Shashkov.
      SEMICONDUCTOR THERMISTORS.
      Inzh.-fiz. zhur. No. 1, 124-6 (1960).
      (Monthly Index of Russian Accessions 13, 1465 (1960)).

      A review, by B.S. Sotskov, of book of this title.

155. Voltz, Sterling E. (to Houdry Process Corp.).
      TREATING CHROMIC OXIDE.
      U.S. 2,714,054, July 26, 1955.
      (C.A. 49, 12955a).

      A semiconducting resistor with negative temperature coefficient is
      made by the following process: Cr_2O_3 is precipitated from $Cr(NO_3)_2$
      solutions with NH_4OH, washed, and dried at 110° for 8 hours. The
      precipitate is heated in N at 350° and then in O (5 liters/hour flow)
      at 350-500° for 2 hours. A further optional treatment in H at 350°,
      which increases the resistance and decreases the temperature coef-
      ficient, may be used to adjust the resistance.

156. Walter, Paul
      NOVEL OXIDE LAYER RESISTOR WITH NEGATIVE TEMPERATURE COEFFICIENT.
      Elektrotech. Z. A78, 500-4 (1957).
      (C.A. 52, 12354b).

      Solutions of hydrolyzable Cd, In, or Sn salts decompose upon contact
      with a hot ceramic carrier body and form semiconducting coatings
      (Ger. 908,882; U.S. 2,564,706 (C.A. 46, 228b)). The resistor bodies
      consist of a ceramic tube, the conductive coating, and the end leads
      (or sleeves), the latter tightened upon a silver paint layer. The
      resistive coating is a mixed oxide of Sn^{4+} and Sb^{3+} (Glang, Thesis,

Tech. Univ. Darnstadt <u>1955</u>). This layer has excellent adhesion and
the hardness of quartz. It is also protected through an insulating
lacquer. The carrier must be above 400° to coat it through spraying,
dipping, or vaporizing. Pure SnO_2 layers have about 200 ohms/sq. cm.
resistivity in an arbitrary standard, which decreases to about 12
ohm/sq. cm. with 1.3 weight % Sb_2O_3 to increase nearly lineraly with
more Sb_2O_3 (about 300 for 14% Sb_2O_3). Temperature coefficient can
be controlled between +0.1 and -1.6%/degree.

157. Weichman, F.P.
OPTICAL AND ELECTRICAL PROPERTIES OF CuO.
<u>PB-140,973</u> (1958).
(OTS <u>Selected</u> <u>Bibliographies</u> - <u>Semiconductors</u>).

158. Weil, L., J. Peretti, and A. Lacaze.
A ZINC OXIDE RESISTANCE THERMOMETER.
<u>Compt</u>. <u>rend</u>. <u>237</u>, 974-5 (1953).
(<u>Physics</u> <u>Abstracts</u> <u>57</u>, No. 2377 (1954)).

A layer of Zn is applied to a ceramic base by a vacuum technique
and connected to the oxide by heating at 400-450° C. in air or oxygen.
Stability is said to be better than that of colloidal graphite and
the accuracy 0.01 against 0.1° for graphite. In the région of 2° K.
the resistance varies by about 10% per degree.

159. Weise, E.K., and B.P. Lathi (Electrical Engineering Researcn Lab,
University of Illinois, Urbana).
ABOUT THE EQUIVALENT CIRCUIT OF THERMISTORS.
<u>AD-148,029</u>, Nov. 1, 1957.
(<u>Astia</u> <u>Bibliography</u>).

An equivalent circuit for thermistors was developed and the elements
were determined for a commercial bead type, both for alternating
current and for direct current transients. The circuit contains an
inductance for which values of several thousand henries were found.
The dependence of the circuit elements upon the position of the
operating point on the characteristic, upon frequency, and upon out-
side parameters, as voltage and series resistance, was determined.
For a particular bead type thermistor critical frequenaies of about
1 cps at an operating point with a current of 1 ma and of about 3.5
cps at 2 ma respectively were found. At these frequencies the therm-
istor displayed the behavior of a pure inductance in producing a
phase shift of exactly 90° between voltage and current. Other inves-
tigators used the same equivalent circuit previously. Their considera-
tions and data were compared with the findings of this work which
shows progress over the earlier investigations especially in demon-
strating the limits of the applicability of the equivalent circuit
assumed.

160. Weise, E.K., and J. Reynolds (Electrical Engineering Research Lab.,
     University of Illinois, Urbana).
     GRAPHICAL EXTRAPOLATION OF VOLTAGE CURRENT CHARACTERISTICS OF THERM-
     ISTORS.
     AD-148,028, Dec. 1, 1957.
     (Astia Bibliography).

     It was found that at each point of the voltage current characteristic
     of a thermistor the rise of temperature above the environmental tem-
     perature is directly proportional to the wattage. Using this relation,
     a simple graphical extrapolation method was derived. By it, any num-
     ber of characteristics at arbitrary environmental temperatures can be
     found if two characteristics and the respective environmental tempera-
     tures have been measured. The limits of the method are discussed.

161. Weise, Erwin K.
     PRINCIPLES OF THERMISTOR APPLICATION.
     AD-148,030, Dec. 15, 1957.
     (Astia Bibliography).

     Log R vs. 1/T curves are plotted for $CaTiO_3$ treated in a special way
     of gradual removal of a certain amount of O from the lattice by
     holding the samples for about 30 minutes in H at various temperatures
     from 1000-1500° C. The properties can also be varied by using dif-
     ferent raw materials; e.g., by mixing several oxides and sintering
     at elevated temperature. Non-linear curves can arise from using
     mixture of different raw materials not forming compounds.

162. Weise, E.K.
     ALIGNMENT CHART FOR RESISTANCE-TEMPERATURE CHARACTERISTICS OF THERMIS-
     TORS.
     AD-148,145, Jan. 20, 1958.
     (Astia Bibliography).

     The relation of resistance (R) ohm and temperature T (°C) is a straight
     line for many commercial thermistors if plotted as log R vs. 1/T or
     log R = K_1 + K_2T and if K, log A and K_2 = B, this becomes log R = log A
     + B/T, R = $A.e^{\frac{B}{T}}$. A plot of log resistance vs. reciprocal absolute
     temperature gives β (slope) and A (vertical axis intercept). The
     temperature coefficient of resistance α (% per degree) = $\frac{1}{R}$ X $\frac{dR}{dT}$ X
     100 or α = $\frac{-B}{T^2}$ X 100. A plot giving this at various temperatures is
     given.

*163. Weise, Erwin K., Willibald Jentschke, and True W. Robinson (U.S. Air
     Material Command).
     THERMISTORS AS TOOLS IN RESEARCH AND DEVELOPMENT.
     PB-100,655 (mi. $2.25, Ph $5.00).
     (Bibliography of Technical Reports 14, 73 (1950)).

     This report introduces the reader to the physical properties, theo-
     retical considerations, applications and current international pro-
     duction possibilities of thermistor type of semiconductors...

*164. Weise, Erwin.
TECHNISCHE HALBLEITER-WIDERSTÄNDE (Technical application of semi-conductor resistances).
PB-52,381 (mi. $2.50).
(Bibliography of Scientific and Industrial Reports 5, 199 (1947)).

This book discusses "semi-conductor resistances." The first chapter elaborates on various types of such resistors that are already in practical use, to wit: (1) The "Urdox resistor" made by Osram A.G. of Berlin; (2) the "Hot conductor" made by Siemens & Halske A.G. of Berlin-Siemensstadt; (3) the "Starto tube" made by N.V. Philips of Eindhoven, Holland; and (4) the "Thermistor" made by the Western Electric Co. of New York. The second chapter deals with the physical properties of semiconducting resistances, whereas the third chapter discusses in detail their practical application. The following uses are listed and described by the author: (1) Resistance thermometers, (2) damping and retardation resistances, (3) cathode- and capacitor-protecting resistances, (4) starting resistances, (5) retardation relays, (6) regulation of electric machines, (7) regulation of arc lamps, (8) bridge resistors, etc. Drawings, graphs, and a bibliography are included. In German.

165. Weise, E.K. (University of Illinois, Urbana).
BASIC AND APPLIED RESEARCH ON SEMICONDUCTORS.
PB-134,716 (mi. $4.80, Ph $13.80, order from Library of Congress).
(U.S. Government Research Reports 30, 351 (1958).

...Sintered samples of Mg_2TiO_4, $MgTiO_3$, $MgTi_2O_5$, $CaTiO_3$, $SiTiO_3$, and $BaTiO_3$ were measured at temperatures between -190°C. and +1500° C. in inert atmospheres. The electrical conductivity was measured between -900° and +1500°. Between +20° C. and -190° C. the Hall effect was measured...Investigations of the resistance-temperature characteristics, the voltage-current characteristics, and the equivalent circuit of thermistors are discussed.

166. Weise, ...
FINAL REPORT ON BASIC AND APPLIED RESEARCH ON SEMICONDUCTORS.
AD-154,200 (AFOSR-TR-58-50), Contract No. AF 33(038)-12644.
(Semiconductor Abstracts VI, No. 587 (1958)).

Electrical conductivity from -190° to +1500° was measured for Mg_2TiO_4, $MgTiO_3$, $MgTi_2O_5$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ in inert atmosphere; Hall effect was determined from -190° to +20°. N-type donors were introduced by partial H_2 reduction. Magnetic susceptibilities, conductivities, Hall data, and electron mobilities were determined for the berthollides. Thermistor properties are discussed.

167. Wejnarth, Axel R.
COMPOSITION OF SILICON CARBIDE ELECTRICAL-RESISTANCE UNITS.
U.S. 2,412,373-4-5-6, Dec. 10, 1946.
(C.A. 41, 1053a).

Addition agents incorporated into Si carbide mixes before sintering
may be one of the group Cr carbide, Cr nitride, Cr silicide, and Cr
boride, together with one of the following metals, combined with any
of the above anions: Mo, W, Ti, and V. The resulting electrical-
resistance units have improved resistance at high temperatures. The
composition also affects the resistance-temperature characteristics.

168. Western Electric Co., Inc.
ELECTRIC CONTROL SYSTEM.
Brit. 465,923, May 19, 1937.
(C.A. 31, 7773²).

Ag_2S resistance units are used to control the gain of an amplifier
or compensate for variations in the resistance of transmission lines.
The units have high negative temperature coefficients...

169. Westinghouse Electric Corp.
THERMISTOR (CONSISTING OF CERAMIC BODIES HAVING A HIGH POSITIVE
TEMPERATURE COEFFICIENT OVER A RANGE OF TEMPERATURES).
Brit. 864,845, Apr. 5, 1961.
(Foreign Patent Abstract Bulletin, No. 81, Aug. 2, 1961).

Thermistor consisting of a ceramic body and electrodes applied thereto
is described, the body comprising essentially the fired product of
(a) a total of 1 mole of at least 1 oxide selected from the group TiO_2,
ZrO_2, Nb_2O_5 and Ta_2O_5, and (b) a combined total of (1) a total of up
to 0.999 mole of at least 1 oxide from the group BaO, PbO, and SiO,
and (2) a total of from 0.0001 mole to the limit of solubility of a
trivalent substitutional impurity of at least 1 rare earth metal
fitting the crystal lattice, the body being initially fired in an oxi-
dizing atmosphere at a temperature of at least 1000° C. for a period
of hours. A typical fired product comprises $YxBa(1-x)TiO_3$ (where x
has a value of 0.005–0.02).

170. Westinghouse Electric Corp.
CERAMIC MEMBER HAVING A MARKED POSITIVE TEMPERATURE COEFFICIENT OF
ELECTRICAL RESISTANCE OVER A SELECTED RANGE OF TEMPERATURES.
Brit. 864,846, Apr. 5, 1961.
(Foreign Patent Abstract Bulletin, No. 81, Aug. 2, 1961).

Ceramic member comprising the fired product having the general formula:
$MxBa(1-x)ZryTi(1-y)O_3$ is described, where M represents at least 1 rare
earth metal from the group consisting of Y and Ce, x has a value of
0.003-0.03 and y, a value of 0.01-0.25, the member being initially
fired in an inert atmosphere to sinter it and thereafter fired in an
oxidizing atmosphere. Compositions of the formula $Y_{0.015}Ba_{0.985}$
$Zr_{0.20}Ti_{0.80}O_3$ were found to have a resistance of 1000 ohms at 45° C.,
the positive temperature coefficient being so large that in the suc-
ceeding 25°, the resistance rose to over 10,000 ohms.

171. Wisely, Harriet R.
      AN EXHAUST GAS TEMPERATURE THERMISTOR BODY FOR THE RANGE 1500°F. TO
      3500°F.
      AD-110,722, Jan. 1957; AD-53,656, Nov. 1954.
      (Astia Bibliography).

      Materials tested having melting points in excess of 3500°F. were
      Al_2O_3, spinel ($MgO.Al_2O_3$) with and without addition of stabilized
      ZrO_2, $CaZrO_3$, MgO with addition of CeO_2, BeO with Al_2O_3 and ZrO_2 or
      ThO_2 additions. Among the compositions tested, the 99% Al_2O_3 body
      most nearly followed the desired resistivity vs. temperature values.

172. Wisely, H.R. (Rutgers Univ., New Brunswick, N.J.).
      RESISTIVITY CHARACTERISTICS OF SOME CERAMIC COMPOSITIONS.
      Am. Ceram. Soc. Bull. 36, 133-6 (1957).
      (C.A. 51, 13338d).

      The electrical resistivity of a number of ceramic compositions were
      determined, 1000-2000°F., in an effort to obtain a thermistor material
      suitable for temperature measurements in the exhaust gases of jet
      engines. Promising materials were subjected to tests of stability
      on prolonged heating in air at 1800°F. and under alternately oxidizing
      and reducing conditions at temperatures up to 2000°F. Compositions
      in the system K_2O-Al_2O_3-SiO_2 (K_2O 5-15, Al_2O_3 40-75, SiO_2 20-48 weight
      %) showed linear relations between log ρ and 1/T and resistivities
      varying from 10^5 to 10^{-6} ohm-cm. at 100°F. to 10^3 to 10^4 ohm-cm. at
      2000°F. Compositions in the system Li_2O-Al_2O_3-SiO_2 showed lower
      resistivities but higher temperature coefficients.

173. Woodbury, H.H., and W.W. Tyler.
      PROPERTIES OF GERMANIUM DOPED WITH MANGANESE.
      Physical Reviews 100, 659 (1956).

      The temperature dependence of the electrical resistivity and Hall
      coefficient in p- and n-type manganese doped Ge crystals indicates
      that Mn introduces 2 acceptor levels in Ge at 0.16 ±0.01 e.v. from
      the valence band and 0.37 ± 0.02 e.v. from the conduction band...
      Comparison is made with other fourth row metals (Fe, V. Co, and Ni)
      as impurities in Ge.

174. Yahia, J., and H.P.R. Frederikse (National Bureau of Standards).
      TEMPERATURE DEPENDENCE OF THE RESISTIVITY, HALL COEFFICIENT, AND
      THERMAL POWER IN Ti_2O_3.
      Bull. Am. Phys. Soc. Sec. II, 5, 407 A (1960).
      (Solid State Abstracts 1, No. 7309 (1961)).

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      * Photocopy available.

Information on the following thermistors, supplied by the manufacturers at our request, is available:

(1) Atkins Technical Inc., Cleveland, Ohio.

"Thermophil" thermistors offering stability, interchangeability, accuracy of 0.2% to 0.7% of total overlapping scale range, a temperature range of -148° to +845° F. or -100 to 450° C. on overlapping scales are based on "the change in electrical resistance of a special Germanium alloy (thermistor)." All probes are interchangeable between instruments of the same type. The heat sensing thermistor has a resistance of 50,000 ohms at room temperature.

(2) Globar Plant, The Carborundum Co., Niagra Falls, New York.

Globar thermistors B, F and H are non-linear (negative temperature coefficient) resistors which offer a range of temperature coefficients from 0.3% per degree C. to 5.1% per degree C. at 25° C.

Type B have a resistance at 25° of 10-100,000 ohms, a temperature coefficient β of 225-470° and % change per degree C. of .25-.53; type F, resistance 10-100,000, β = 1200-2150, % per degree C. = 1.35-2.40; type H, resistance 3150-500,000, β = 3000-4600, % per degree C. = 3.40-5.20. The thermal time constant is 15 seconds to 3-5 minutes; stability is good.

Globar also makes a positive temperature coefficient thermistor, sensitive between -30 and 100°C. for which temperature vs. percent resistance at 37.8°C. curve is given.

(3) Fenwal Electronics, Framingham, Massachusetts.

"Thermistors are semiconductors made by sintering mixtures of metallic oxides such as Mn, Ni, Co, Cu, Fe and U. Various mixtures of these metallic oxides are formed into useful shapes. Their electrical characteristics may be controlled by varying the type of oxide used and the physical size and configuration of the thermistor."

β value for Fenwal Electronics Thermistors is approximately 4000, α, the temperature coefficient of resistance, is as high as -5.8% at room temperature, resistance values of 300 ohms to 100 megohms for beads, 5 to 10,000 ohms for discs, and 1000-150,000 ohms for rods can be obtained.

(4) Ferroxcube Corp. of America, Saugerties, New York.

"NTC" resistors have a high negative temperature coefficient of resistance (-3 to -6 1/2 % per °C.). The resistors consist of a disc of semiconductive ceramic material, both faces of which are covered with a layer of silver serving as an electrode. They are available in five different nominal values of resistance at 25° ranging between 4 and 1300 ohms. Value of β varies from 3300-5700.

Ferroxcube also makes "VDR" or voltage-dependent resistors.

(5) Magnetic Materials Section, General Electric Co., Erdmore, Michigan.

General Electric thermistors are made in two material grades and three main types: rods, discs and washers. The raw materials — Mn, Ni, and Co oxides — are milled and mixed in accurate proportions. Suitable binders are added and the units are pressed or extruded to the desired shapes. Thermistor elements are then sintered under carefully controlled atmospheric and temperature conditions to produce a hard ceramic-like material. The properties are as follow:

Material	Sp. Resistance at 25° C. ohm-cm.	β 25°-75° C. °K.	Thermal Resistivity °C. x in.^{2} watts x in.	Thermal Conductivity BTU x in. °F. x ft^2 x hr.
1	$2100 \pm 10\%$	3965 ± 55	29.4	9.4
2	$300 \pm 10\%$	3530 ± 80	20.2	13.5

Temperature coefficient of resistance at 25° C. = -4 to -4.5% per °C.

(6) Gulton Industries, Inc., Metuchen, New Jersey.

"Glennite Thermistors" are ceramic temperature-sensitive resistors. Exhibiting high negative coefficient of resistance, these semiconductors possess resistance values which may vary by a ratio of 10,000,000 to 1 from -100°C. to +450°C. They are available in a resistance range from ohms to megohms and their thermo-resistive characteristics, coupled with excellent stability and high sensitivity in a small, rugged unit, present endless possibilities in circuit design. The temperature coefficient of resistance given varies from -3.9 to -6.8% for wafers, -3.9 to -5.4% for beads, β = 3400-4115.

(7) Keystone Carbon Co., St. Marys, Pennsylvania.

NTC Resistance Units are formed of metallic compounds, heat treated, contacted and aged for maximum stability and possess the unique characteristic of a large negative change in resistance with respect to temperature. The temperature coefficient is -1.2 to -5% per degree C. They operate at -80 to 150° C.

(8) Kidde Thermistors.

Type K — β = 3100°K., time constant = 18 seconds, resistance at 25° = 1-100 K; Type D — β = 3100°K., time constant 26 seconds, maximum operating temperature 150°C., resistance at 25°C. 100 ohms to 100 K ohms.

(9) Sperry Microwave Electronics Co., Clearwater, Florida.

.Miraline thermistors are actually small high resistance ceramic beads supported between two parallel wires...For greater rigidity the bead is generally enclosed in glass. The temperature range is -35 to 800°. These thermistors are used for c-w or average power measurement.

(10) Victory Engineering Corp., Union, New Jersey.

Veco thermistors are manufactured in three distinct forms: beads, discs or washers, and rods. All of these types are made of various mixtures of the oxides of Mn, Ni, Co, Cu, U, Fe, Zn, Ti, and Mg. These materials are mixed in proper proportion to provide the required specific resistance and temperature coefficient of resistance for particular applications. These mixtures of oxides are formed into the desired shapes and sintered under accurately controlled atmospheric and temperature conditions. The finished product is a hard ceramic material which may be mounted in a variety of ways depending upon the mechanical, electrical, and thermal requirements.

All Veco thermistors are produced by carefully controlled processes which give them the following characteristics:

1. Extremely high stability.
2. Mechanical ruggedness and excellent shock resistance.
3. Permanent electrical contacts.
4. Wide range of resistance, temperature coefficient, and power dissipation.
5. Unlimited life when operated within maximum temperature ratings.
6. Small, compact size.

Thermistor material No. 1 is composed of oxides of Mn and Ni and has a temperature coefficient of resistance of -4.4% per °C. at 25°C. and is recommended when comparatively high resistance and an extremely high temperature coefficient are desired.

Thermistor material No. 2 is composed of oxides of Mn, Ni, and Co and has a temperature coefficient of resistance of -3.9% per °C. at 25° C. and is used in applications where comparatively low resistance and a moderate temperature coefficient are desired.

There are many other special Veco thermistor mixes now being used for thermistors requiring exceptionally high or low resistance or where special temperature coefficients of resistance are required.

Specific resistances ranging from 100 to 450,000 ohm-cm. at 25°C. have been produced which gives engineers a wide latitude in the design of equipment utilizing Veco thermistors. For example, Veco thermistors are now being produced with a temperature coefficient of resistance as high as -5.8% per °C. at 25°C., while that of platinum is only +0.36° per °C.

Other companies contacted were:

(11) Bart Labs, Newark, New Jersey — no reply.

(12) Bendix Corp., Frieg Instrument Division, Baltimore, Maryland — who no longer manufacture thermistors.

(13) Cornell-Dublier Electric Co., South Plainfield, New Jersey — no reply.

(14) Electro-Impulse Laboratory, Inc., Red Branch, New Jersey — who do not make thermistors.

(15) Marshal Instrument Co., Van Nuys, California — who make a thermistor
actuated electronic thermometer.

(16) Precision Thermometer and Instrument Co., Philadelphia — who do not make
thermistors.

(17) Thermo-Products Co., Inc., Milwaukee, Wisconsin — no reply.

Thermistor Applications

A large number of abstracts on specific applications have been collected
and are available on request. However, it is felt that the following tabula-
tion, abstracted from the Veco "Data Book" indicates adequately the variety
of these applications.

APPLICATIONS FOR VECO THERMISTORS IN VARIOUS INDUSTRIES.

Communications

Ambient Temperature Compensation
Time Delay Devices
Voltage Regulators
Overload Protectors
Remote Controlled Resistance
Switching Devices
Negative Resistors
   Oscillators
   Amplifiers
   Transmission Networks
Amplitude Stabilized Oscillators
Power Indicators
Compressors and Expanders
Volume Limiters
Automatic Gain Regulators

Mining and Metallurgy

Fire Protection and Safety Devices
Gas Detectors
Pyrometry
Quality Control
Time Delay Devices
Geological Temperature Surveys
Calorimetry
Local and Remote Temperature
 Measurement and Control

Manufacturing

Quality Control
Fire Protection Devices
Temperature Measurement and Control
Surge Suppressors
Anemometry
Flow Meters
Differential Temperature Controllers
Vacuum Gauges
Automatic Switching
Time Delay Devices
Voltage Regulators
Pyrometry

Chemical and Food Processing

Calorimetry
Local and Remote Temperature
 Indication
Chemical Analysis
Automatic Temperature Control
Refrigeration Control
Pyrometry
Vacuum Gauges
Temperature Compensation
Gas Detectors

Transportation

Engine Temperature Measurement and
  Control
Flow Meters
Switching and Signalling Devices
Differential Temperature Controllers
Fire Protection and Safety Devices
Test Equipment
Aircraft Cabin Temperature Control
Meterological Equipment
Wing Temperature Measurement for Aircraft
Aircraft Anti-icing Control

Housing and Household Appliances

Automatic Switches
Fire Protection Devices
Automatic Room Temperature Control
Air Conditioning Systems Control
Gas Detectors
Furnace Controls
Oven Temperature Control
Refrigeration Control

Public Utilities

Voltage Regulation
Time Delay Devices
Warning Devices
Gas Detectors
Flow Meters
Anemometry
Chemical Analysis and Control
Power Indicators
Temperature Compensation of Instru-
  ments
Switching Devices
Calorimetry
Pyrometry

Medical and Scientific

Temperature Measurement of Blood
  in the Human Body
Subcutaneous Skin and Muscle
  Temperature Measurement

Instrumentation

Power Indicators
Pyrometry
Meteorological Equipment
Vacuum Gauges
Temperature Compensation

In addition to the uses mentioned here, attention should also be called
to the interest in thermistors as bolometers, indicated by a large number of
references in various government reports.

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